

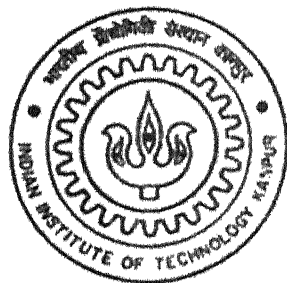
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# **ELECTROREMEDIATION OF SOIL CONTAMINATED WITH A DICHROMATE LIXIVIAN**

by

**Manindra Manna**



**DEPARTMENT OF MATERIALS AND METALLURGICAL ENGINEERING**

**Indian Institute of Technology Kanpur**

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बुद्धोत्तम काशीनाथ केचकर पुस्तकालय  
भारतीय प्रौद्योगिकी संस्थान कानपुर  
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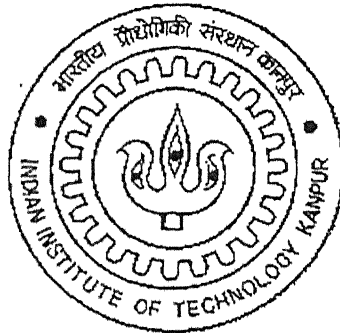
# **ELECTROREMEDIATION OF SOIL CONTAMINATED WITH A DICHROMATE LIXIVIAN**

A Thesis submitted  
in Partial Fulfillment of the Requirements  
for the degree of

**MASTER OF TECHNOLOGY**

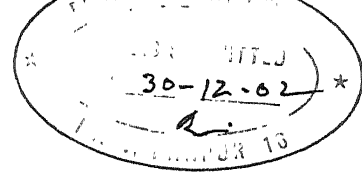
By

**MANINDRA MANNA**



**DEPARTMENT OF MATERIALS AND METALLURGICAL  
ENGINEERING**

**INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
DECEMBER, 2002**



## **CERTIFICATE**

This is to certify that the investigation on "Electroremediation of soil contaminated with a dichromate lixiviant" has been carried out by Mr. MANINDRA MANNA (Roll No-Y020604) dissertation under our guidance and it has not been submitted elsewhere for a degree.

(Dr. R. Shekhar)

Professor

Department of Materials and Metallurgical Engineering  
Indian Institute of Technology, Kanpur

(Dr. S. Sarkar)

Professor

Department of Chemistry  
Indian Institute of Technology, Kanpur

Dated: December, 2002

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Manindra Manna

03/02/03

*dedicated to my parents.....*

## Abstract

Chromium is released from a variety of sources such as tanneries, electroplating units and chemical industries. Because of its toxic nature and widespread use, contamination of soil with chromium, especially Cr(VI), has become a major environmental problem. Electroremediation experiments have been carried out on synthetic kaolin and Kanpur soil contaminated with dichromate lixiviant. The objective of this study has been to determine the kinetics of electroremediation and the associated rate controlling mechanism.

The soil-lixiviant mixture, containing 500 mg Cr(VI)/kg soil, was compacted in a cylindrical tube, 15.26 cm long x 3.8 cm diameter. Experiments were conducted by applying three voltages (25, 15 and 5 volts) to disc-shaped graphite electrodes, at the ends of the section, for 6 days. Analysis was done to determine the (i) rate of remediation of chromium from soil and (ii) the extent of unremediated chromium.

A maximum of 36.6% chromium was removed from kaolin at 25 volts. Approximately 20% chromium was removed in the first 20 hours. Thereafter, there was a drastic reduction in chromium removal rate. After 124 hours, only 36.6% of Cr(VI) was removed from kaolin. Migration of the acid and base fronts leading to acid-base neutralization adjacent to the cathode end of kaolin appears to be the rate controlling step. Removal of chromium from Kanpur soil was more efficient than in kaolin, with approximately 85% chromium being removed in the first 20 hours. The difference in the remediation efficiency in kaolin and Kanpur soil can be attributed to the nature of the soil; the former is weakly acidic (pH = 5.5), while the latter is basic (pH = 10.5). Moreover, Kanpur soil is a strong basic buffer.

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# CHAPTER I

## INTRODUCTION

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### Introduction

Over the years, industrial wastes have been dumped indiscriminately, without resorting to proper waste management techniques. Toxic heavy metals in solid wastes are leached by rainwater, which in turn contaminates the soil as it migrates through the subsurface. The heavy metal-contaminated soil is a recipe for disaster since it contaminates not only the ground water supply but also the crops grown on this soil [1]. Early remedial actions for contaminated soil consisted primarily of excavation and removal of the contaminated soil from the site and disposal at a landfill. More emphasis is now placed on **insitu** treatment of soil. Electro kinetic decontamination is perhaps one of the most promising in situ soil decontamination process capable of removing heavy metals and organic contaminants from soil feasibly. Cr (VI), is a toxic species, released from a variety of sources such as tanneries, electroplating units, and chemical industries. In order to protect public health and environment, considerable attention has been focused on the development of cost effective, in situ technologies for treating chromium contaminated soils.

Because of their cost-effectiveness, there has been an increasing interest in situ treatment techniques, without excavation of the soil. One possible method of removing heavy metals is the percolation leaching technique [2,3], extensively practiced for the heap leaching of lean non-ferrous ores such as those of copper and silver. Soils are typically heterogeneous, and "pressure-driven" flushing processes, as in percolation leaching, invariably channel the fluid through the largest pores, leaving the smaller pores untouched. However, the adsorption of heavy metal ions mainly happens in the smallest pores due to the stronger electrostatic forces in these pores. that is, the percolation leaching technique would only be effective in soils of high "permeability."

A relatively new and potentially important in situ technique has emerged in which a **dc electric field** is applied across electrode pairs placed in the ground. The contaminants in the liquid phase in the soil are moved under the action of the field to wells where they are then pumped out. The principle mechanism by which contaminant transport takes place under the action of an electric

field is electroosmosis and electromigration. Electroosmosis is only effective in fine-grained soils with micrometer size or smaller pores. Electromigration not dependent on pore size and so is applicable equally to coarse and fine-grained pores. Another important advantages of this electrochemical technique is the high degree of control of flow direction that can be achieved because the materials move along electric field lines that are defined by the electrode placement. A number of laboratory investigations [4-8] and limited field experiment [9] have demonstrated the viability of cleaning heavy metal contaminated soils. These studies have highlighted phenomena that effect cleaning efficiency such as nature of the soil, evolution of pH profile, precipitation and adsorption of heavy metals. Unfortunately, very little attention has been focused on Cr (VI) contaminated soils and none of these studies have focused on an issue of vital importance related to real-life implementation, namely: what is the kinetics, unremediated chromium [10] and associated rate controlling mechanism? Moreover, the source of Cr (VI) was synthetic potassium dichromate. Hence the objective of this investigation has been to demonstrate the efficacy of electrochemically cleaning soil, contaminated with a real life source of Cr (VI). Experiments have been carried out on kaolin and Kanpur soil contaminated with lixiviant obtained from a sodium dichromate plant residue.

### **1.1. Principals of Electrokinetics Soil Remediation**

Electrokinetic soil remediation technology uses a low level direct current, in the orders of milliamps per  $cm^2$  of soil cross-sectional area, to transport and recover species from soils. Upon application of a low level direct current the soil, water-electrolyte system undergoes physicochemical and hydrological changes leading to contaminants transport and removal. The applied electric current (or electric potential difference) leads to electrolysis reactions at the electrodes, acid-base distribution drive by chemical, electrical, and hydraulic potential differences, adsorption/desorption, transport of the pore fluid and ions.

### 1.1.1. Electrolysis Reactions

Application of direct current through electrodes immersed in water induces electrolysis reactions in the immediate vicinity of Electrodes. Oxidation of water at the anode generates an acid front while reduction at the cathode produces a base front by the following electrolysis reactions,



Secondary reactions may exist depending upon the concentration of available species, e.g.,



Where  $E^0$  is the standard reduction electrochemical potential, which is a measure of the tendency of the reactants in their standard states to proceed to products in their standard states, and Me refers to metals. The prevailing of electrolysis reactions at the electrode depends on the availability of chemical species and the electrochemical potentials of these reactions. Although some secondary reactions might be favored at the cathode because of their lower electrochemical potential, the water reduction half reaction ( $2\text{H}_2\text{O} / \text{H}_2$ ) is dominant at the early stages of the process. At the latter stages, the acid front advances towards the cathode carrying  $\text{H}^+$  and other cations. Within the first 100 hours of processing, electrolysis reactions will drop the pH at the anode to below 2 and increase it at the cathode to above 12, depending upon the total current applied [11-12].

### 1.1.2. Change in Soil pH

The acid generated at the anode will advance through the soil towards the cathode. This advance is governed by different transport mechanisms including ionic migration due to electrical gradients, pore fluid advection due to prevailing electroosmotic flow, pore fluid advection due to any externally applied or internally generated hydrolic potential differences, and diffusion due to concentration gradients. The alkaline medium developed at the cathode due to production of  $\text{OH}^-$  will initially advance towards the anode by diffusion and ionic migration; however, the counterflow due to electroosmosis will retard this back-diffusion and migration. The advance of this front-towards the anode will be much slower than the advance of the acid front towards the cathode because of the counteracting electroosmotic flow and also because the ionic mobility of  $\text{H}^+$  is about 1.76 times that of  $\text{OH}^-$ . As a consequence, the acid front dominates the chemistry across the specimen [11-12].

The decrease in pH value in the soil depends on the amount of acid generated at the anode [11-12] and the buffering capacity of the clay.

A partial reduction of Cr(VI) into Cr(III) occurs in soils in the presence of reducing agents even before electrokinetic treatment begins [13].

### 1.1.3. Transport Processes

Application of hydraulic, electric, chemical, and/or thermal gradients to a homogeneous medium of soil-water-electrolyte results in transport of matter and energy. The resulting fluxes of fluid, charge, mass, and/or heat through the soil medium, their changes with time, and their effects on the properties and composition of the soil medium are significant in various geoenvironmental problems.

The fluxes of matter and/or energy through soil-water-electrolyte media could be categorized into two types; uncoupled fluxes and couple fluxes. Direct spontaneous uncoupled fluxes result from application of a potential gradient of the same type of the matter transported (conjugated driving forces). Examples of direct fluxes are fluid transport due to a hydraulic gradient (Darcy's law), charge transport due to an electric gradient (Ohm's law), mass transport due a chemical

gradient (Fick's law), and heat transport due to a thermal gradient (Fourier's law). Coupled fluxes result from transport of matter and/or energy due to a potential gradient of different type than the matter and/or energy transported (non-conjugated driving forces). The nature of the soil-water-electrolyte system with the presence of the diffuse double layer gives rise to a spontaneous coupled transport fluxes. Examples of couple fluxes in soil-water-electrolyte system are water transport due to an electric gradient (electroosmosis), heat transport due to a chemical gradient (Dufour effect), and charge transport due to a thermal gradient (Soret effect).

#### 1.1.3.1. Darcy's Law of Advection

Fluid flow due to a hydraulic gradient,  $J_w^h (LT^{-1})$  is given by Darcy's law as,

$$J_w^h = k_h \nabla(-h)$$

where  $k_h$  is the coefficient of hydraulic conductivity,  $h$  is the hydraulic head ( $h = u/\gamma_w$ ),  $u$  is the hydraulic potential, and  $\gamma_w$  is the unit weight of the pore fluid.

#### 1.1.3.2. Electroosmosis

The Helmholtz-Smoluchowski theory for the electroosmosis is the most commonly adopted theoretical description of fluid transport through soils due to electrical gradients. Similar to the hydraulic conductivity, this theory introduces the coefficient of electroosmotic permeability,  $k_e$ , as the volume rate of fluid flowing through a unit cross sectional area due to a unit electrical gradient.

$$J_w^e = k_e \nabla(-E) = k_e I$$

where  $k_e$  is the electroosmotic coefficient of fluid transport given by,

$$k_i = \frac{k_e}{\sigma^e} \quad \text{where } \sigma^e \text{ is the effective electrical conductivity of the soil medium.}$$

The value of  $k_e$  is widely accepted to be a function of zeta potential, viscosity of the pore fluid, porosity and electrical permittivity of the soil medium. When the soil pores are treated as the capillary tube, the coefficient of electroosmotic permeability is given by,

$$k_e = \frac{\varepsilon \varepsilon_0 \zeta}{\eta} n \quad \text{where } \varepsilon \text{ is the permeability of the medium, } \zeta \text{ is the zeta potential, } n \text{ is}$$

the porosity, and  $\eta$  is the viscosity.

Mitchell [14] in an extensive summary of theoretical and experimental treatise of the zeta potential in colloid science, displays the effect of pH and ion concentration in the pore fluid on zeta potential. The effect of electrolyte chemistry on zeta potential could therefore represented by Kruit[15],

$$\zeta = A - B \log C_0$$

where, A and B are two conatants that are evaluated experimentally, and  $C_0$  is the total electrolyte concentration.

### 1.1.3.3. Fick's Law of Diffusion

The diffusive mass transport of chemical species in a saturated soil medium under chemical concentration gradients is described by Fick's first law,

$$J^d_i = D^0_i \nabla(-c_i)$$

where  $J^d_i$  is the diffusive mass flux of the  $i$ th chemical species per unit cross sectional area of the porous medium,  $c_i$  is the molar concentration of the  $i$ th chemical species,  $D^0_i$  is the effective diffusion coefficient of the  $i$ th chemical species.

#### 1.1.3.4. Electromigration

The migrational mass flux of the free ionic species in the soil pore fluid due to the applied electric field is given by,

$$J^e_i = u^0_i c_i \nabla(-E)$$

where  $J^0_i$  is the migrational mass flux of the  $i$ th species, and  $u^0_i$  is the effective ionic mobility of the  $i$ th species. The effective ionic mobility,  $u^0_i$ , defines the velocity of the ion in the soil pores under unit electric field.

$$u^0_i = n \tau u_i = \frac{D^0_i z_i F}{RT}$$

where  $u_i$  is the ionic mobility of species  $i$  at infinite dilution,  $z_i$  is the charge of the  $i$ th species,  $D^0_i$  is the molecular diffusion coefficient,  $F$  is the Faraday's constant,  $R$  is the universal constant,  $\tau$  is the tortuosity of the soil medium,  $n$  is the porosity of the medium and  $T$  is the absolute temperature.

### 1.2. Source of Cr(VI)

The different source of Cr(VI) which contaminate soil are:

Primary metal producing plants

Metal processing industries such as those involved in electroplating

Distilleries

Tanneries

Thermal power plants

Chemical plants

Municipal sludge

## CHAPTER II

### LITERATURE REVIEW

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Multi-species transport under electric fields is an area that is gaining increasing attention and interest. Species transport mechanism under electric fields are envisioned to-be employed in remediating soils from inorganic and organic species(electrokinetic remediation). Laboratory scale and limited pilot scale studies in elctrokinetic remediation demonstrate that the technique has significant potential. It becomes necessary to gain a better understanding of multi-species transport mechanism both in an effort to critically evaluate the fundamental basis of the processes and also to develop the necessary design/analysis tools in engineering the implemented techniques.

#### 2.1. Previous Soil Remediating Work

Hamed and co-workers [5] investigated the electrokinetic removal of Pb from saturated kaolinite specimens loaded with 118 to 145  $\mu\text{g}$  of Pb(II) per gram of dry soil. 75 to 95% of the adsorbed Pb(II) was removed by this process. The energy requirement was 17 kWh - 35 kWh per ton of soil, or of the order of \$12 per ton of soil, significantly less than the cost of the present techniques that varies between \$30 and \$875 per ton of soil.

Reddy and co-workers [10] conducted electroremediation experiments on three types of soils: glacial till, kaolin and Na-montmorillonite in order to investigate the effect of soil mineralogy on the removal of chromium. Results showed that Cr(VI) removal was most efficient in glacial till, a phenomenon attributed to its buffering capacity that minimised the readsorption of chromium ions. This study has shown that soils which contain high carbonate buffers, such as the glacial till, hinder the development of an acid front, which results in alkaline conditions through out the soil during electro kinetic remediation. However, soil processing low buffer capacity, such as kaolin and Na-montmorillonite, favor the development of an acid front which results in a distinct pH gradient with pH values varying from 2 near the anode to 11 near the cathode.

**Generally**, discrete clay particles have a negative surface charge that influences and controls the particle environment. This surface electric charge can be developed in different ways, including the presence of broken bonds and due to isomorphous substitution [14]. The net negative charge on the clay particle surfaces requires an excess positive charge ( or exchangeable cations) distributed in the fluid zone adjacent to the clay surface forming the diffuse double layer.

Several theories have been proposed for modeling charge distribution adjacent to clay surface. The Gouy-Chapman diffuse double layer theory has been widely accepted and applied to describe the clay behavior.

Electrokinetics is defined as the physicochemical transport of charge, action of charge particles, and effects of applied electric potentials on formation and fluid transport in porous media. The presence of diffuse double layer gives rise to several electrokinetic phenomena in soils, which may result from either the movement of different phases relatives to each other due application of electric field. The electrokinetic phenomena include electroosmosis, electrophoresis, streaming potential, and sedimentation potential. Electroosmosis is defined as fluid movement with respect to a solid wall as a result of an applied electric potential gradient. In other wards, if the soil is placed between the two electrodes in a fluid, the fluid is move from one side to the other when an electromotive force is applied. Electrophoresis is the movement of solids suspended in a liquid due to application of potential gradient. Streaming potential is the reverse of electroosmosis. It defines the generation of an electric potential difference due to fluid flow in soils. Sedimentation (or migration) potential, known as Dorn effect [15], is an electric potential generated by the movement of particles suspended in a liquied.

**DC electric fields** have been used for a number of applications such as improving stability of excavations; stability of fine-grained soils; dewatering of foams, sludges, and dredgings. The principal mechanism involved in these applications was "**electroosmosis**." In an early study Jacobs and Mortland [16] demonstrated that  $\text{Na}^+$  and  $\text{K}^+$  ions can be leached out of clays by electroosmosis. Krizek and co-workers [17] showed that soluble ions content substantially increased in the effluent after electroosmotic consolidation of polluted dredgings. Segal and co-workers [18] discovered that

heavy metals concentration in the effluent after electroosmotic consolidation of sludges. The electroosmotic flow rate is directly proportional to the zeta potential. Vane and Zang [19] investigated the effect of pH on clay particle zeta potential on two different soils, Georgia kaolinite and Wyoming bentonite. The zeta potential for the kaolinite ranged from +0.7 mV at pH=2 to -54 mV at pH=10 while the bentonite zeta potential changed by only 5 mV (-31 to -36 mV).

Pamucku and Wittle [6] and Coletta and co-workers [20] also successfully removed heavy metal from soil. Lageman and co-workers [21] report laboratory experiments where heavy metals Cd, Cr, Ni, Pb, Hg, Cu, Zn and As were successfully removed from agrillaceous sand and river mud.

Puppala and co-workers [22] investigated the feasibility of heavy metal removal from high sorption capacity soil by the use of acetic acid to neutralise the cathode electrolysis reaction and also the use of an ion selective membrane (Nafion) to prevent back transport of  $\text{OH}^-$  generated at the cathode. Acetic acid and Nafion enhancement resulted in better removal efficiencies of lead from a synthetic soil consisting of 40% illite, 8% kaolinite, 5% Na-montmorillonite and 47% fine sand.

Li and Neretnieks [23] countered the problem of metal hydroxide precipitation by placing a tube length of conductive solution, simulating groundwater between the soil and the cathode. However, the length of the conductive solution was relatively large, twice that of the soil being treated. Using this technique, Li and co-workers [7] achieved metal removal efficiencies of 90% with respect to lead (II), cadmium (II) and chromium (III) from sand. Li and co-workers [8] reduced the volume of water needed considerably by placing a cation selective membrane in front of the cathode. Experiments showed that 90% of copper could be removed from sand, and energy consumption was 20 kWh/ton of soil.

Hansen and co-workers [24] investigated the electrodialytic remediation of heavy metal polluted soil, a variant of the conventional electroremediation technique. This method combines electrodialysis with the electromigration of ions in the polluted soil. The cell consists of three compartments; two electrode compartments and a soil compartment placed between them. The catholyte is separated from the soil by a cation exchange membrane and the anolyte is separated from the soil by an anion exchange membrane. When the current is passed through the cell, no current carrying ions can pass from the electrode compartments into the soil due to the ion exchange

membranes, while ions can be transported from the soil into the electrode compartments. In this system current is thus prevented from being wasted in carrying highly mobile ions from one electrode compartment, through the soil, into the other electrode compartment. Hansen and co-workers [24] carried out experiments on soil samples from three contaminated sites, with pollution originating from a wood preservation factory (Cu, Cr), a chlor-alkali plant (Hg), and a copper rolling mill (Cu, Pb, Zn). The electrodialytic remediation process was very effective in removing copper and to a certain extent chromium. However, only 23 % of the Hg could be removed. From the experiments it was also seen that the effect of pH on the desorption of heavy metals from the soil is important. In particular, copper, zinc, and lead seem to desorb at acidic pH values between 3 and 4. Chromium needs a pH of around 2.5 for desorption.

Very few studies on pilot-scale and actual field experiments have been reported. Acar and Alshawabkeh [25] studied the feasibility and efficiency for removing lead at pilot scale in three 1 ton Georgia kaolinite specimens. Subsequent to 2,950 h of processing and an energy expenditure of 700 kWh/m<sup>3</sup>, 55% of the lead removed across the soil was found precipitated within the last 2 cm close the cathode. 15% of lead was readsorbed in the soil, while 20% was found precipitated on the fabric separating the soil from the cathode compartment. Lageman and co-workers [21] report four field experiments of electroremediation of heavy metal contaminated soil carried out in the Netherlands.

Significant changes in exchangeable and soluble fractions occurred after electrokinetic treatment [26].

**Closed paint factory:** Site: 70 m x 3 m x 0.5 m deep. Initial lead (300 - 5000 PPM) and copper (500 - 1000 PPM) concentrations reduced by 70% and 80% respectively. after current for 10 hours per day for 43 days.

**Galvanising unit:** Site : 15 m x 6 m x 1 m deep. Average zinc concentration reduced from 2410 PPM to 1620 PPM in eight weeks. Low removal rate of zinc was attributed to the high buffering capacity of the soil and by the presence of ammonia and ammonium chloride in the soil.

**Timber impregnation plant:** 65 days of treatment reduced arsenic levels in the soil decreased from 400 - 500 PPM to less than 30 PPM. An interesting observation was that any metallic object greater than 10 cm interfered with the flow of electric current rendering remediation less effective.

**Temporary landfill** filled with soil and sludge contaminated with cadmium and other heavy metals: 2300 m<sup>3</sup> of soil was remediated and cadmium was reduced from a maximum value of 3400 mg/kg to less than 40 mg/kg. For the field experiments the electrode configuration consisted of

horizontal cathodes and a row of vertical anodes. Energy consumption was reported to be 38 kWh/ton of soil for the paint factory project and 160 kWh/ton for the galvanising plant project.

Under certain conditions, electroosmosis will have a significant role in electrokinetic soil remediation. Several theories are established to describe and evaluate water flow by electroosmosis. Helmholtz-smoluchowski model is the most common theoretical description of electroosmosis and is based on the assumption of fluid transport in the soil pores due to transport of the excess positive charge in the diffuse double layer towards the cathode.

## **2.2. Objectives of the Present Work**

1. Determine rate controlling mechanism for the remediation of synthetic kaolin and Kanpur soil contaminated with dichromate lixiviant.
2. Effect of voltage and nature of soil in electroremediation processes.

# CHAPTER III

## EXPERIMENTAL APPARATUS & PROCEDURE

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### Introduction

1. Electroremediation of hexavalent chromium contaminated soil was carried out by one-dimensional technique. This section deals with the experimental set up and parameter used in the experiment.

#### 3.1.1. One Dimensional Set-up

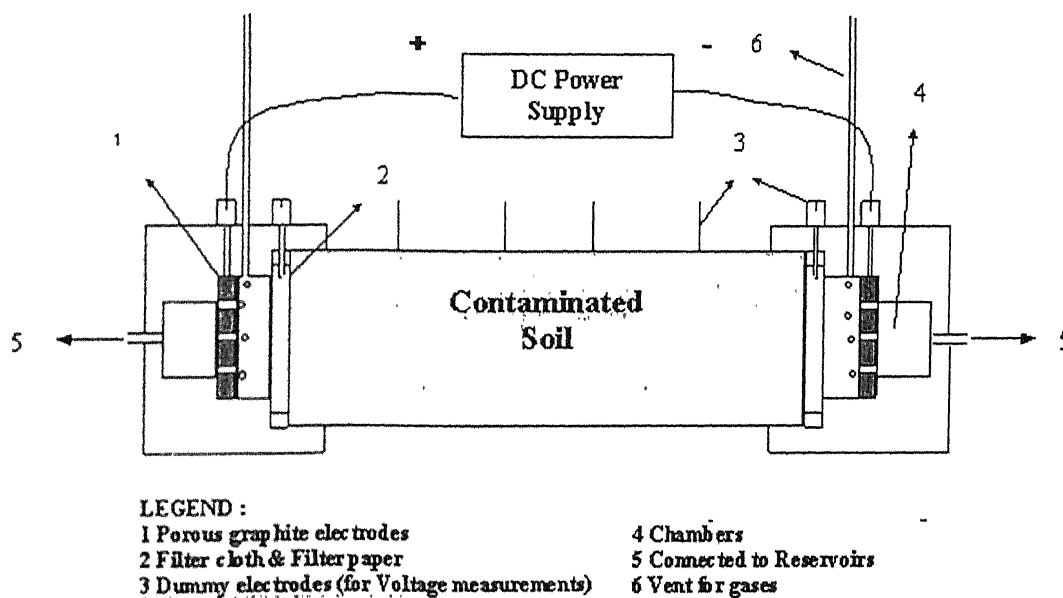


Fig. 1 Schematic diagram of the experimental set-up.

Fig. 3.1 is a schematic sketch of the 1-D experimental apparatus. A cylindrical Perspex tube, 15.25 cm long and 3.81 cm in diameter, was used to house the contaminated soil. Two Perspex caps containing the graphite electrodes 4 cm in diameter and 1 cm in thickness and

liquid compartments 4.8 cm and 5.8 cm in diameter at different 2 sections, with provision for gas venting were screwed on to both ends of the Perspex cylinder. Holes were drilled in the graphite electrodes for (i) the passage of ions from the soil to electrode compartments and (ii) to accommodate bulk electrolyte flow by electroosmosis. In our earlier set-up, the soil was in direct contact with the electrodes. However, blockage of electrode holes by electrolytically-generated gases, at the soil-electrode interface, prevented the passage of ions from the soil into the electrode (anode) compartment as well increased the resistance. To overcome this deficiency, the soil was separated from the electrodes by pushing the electrodes into the compartments and the vent was kept in front so that the gas bubbles generated can escape from vent. The soil, in turn, was supported by a porous canvas cloth and filter papers. The ends of the two Perspex caps were connected to two reservoirs, which served as an “electrolyte source” for electroosmosis. Four dummy electrodes were inserted in the soil to determine the voltage distribution along the length of the reactor. Inter distance between any two dummy electrode was 2.1 cm.

### **3.2. Experimental Procedure**

Total experimental process consist of different experimental step (1) Lixiviant preparation (2) Experimental set up preparation (3) Soil preparation & compaction (4) Monitor current, voltage & electroosmotic flow rate with time(5) Sampling (6) Soil extrusion (7) Cr(VI) analysis (8) Moisture, Total Cr(VI) and pH analysis (9) Adsorption studies.

#### **3.2.1. Lixiviant Preparation**

Sodium dichromate residue was collected from a sodium dichromate plant, was first ground in a ball mill and then sieved to -100 mesh size. The Lixiviant was obtained by a 3-stage sequential leaching in a shaker of the dichromate residue in double distilled water. Duration of each stage of leaching was 2 hrs after that the leaching period, solution was centrifuged. Initial pH of the lixiviant was 11.3.

### 3.2.2. Experimental Set up Preparation

After each experiment it is necessary to ready the set up for another experiment. At first cleaned up the set up in tap water. Rings were covered with porous canvas cloth by using fevistick to support the slurry materials. Both electrodes and rings were tightened by steel screws, above the canvas cloth one new round shape 542 filter paper was placed to protect soil movement in the chamber. Above the thread of the steel screws grease and at end of the thread washer were given to hinder rusting of the steel screws and out ward water flow consequently.

### 3.2.3. Soil Preparation and Compaction

<u>Composition of Kanpur soil</u>		<u>Composition of Kaolin</u>
Mn	0.03 %	Heavy metals as lead (0.002 %)
Zn	0.01 %	Chloride (0.02 %)
Cr	0.04 %	Sulphate (0.05 %)
Fe	3.83 %	Maximum impurities soluble in acid
Co	0.02 %	( as sulphate)
Ni	0.003 %	
<u>Composition of dichromate residue</u>		
Fe = 8.945 (Wt %), Co = 0.055 (Wt %), Ni = 0.063 (Wt %), Cu = 0.0075 (Wt %)		
Mn = 0.13 (Wt %), Zn = 0.057 (Wt %), Cr = 4.0 (Wt %)		

Soil is mixed thoroughly with requisite volume of lixiviant solution to achieve the desired Cr(VI) concentration of 500 mg/kg soil. The resulting slurry, with a 60-65 % degree of saturation, was compacted in the Perspex tube by applying 17.34 kg static load from the top with other end closed. Loading time for each layer of compaction was 10 minutes, after each layer of compaction slurry was scratched with screw driver to maintained uniformity with the 2<sup>nd</sup> layer of compaction. Compaction was completed after 5 layer of compaction after that both caps were tightened with the Perspex tube. -ve reservoir and +ve reservoir were connected with the -ve chamber and +ve chamber respectively. Full of chambers and up to 50 ml of the reservoirs were filled with double distil water.

### 3.2.4. Measurements of Current, Voltage and Electroosmotic Flow

A 25 volts constant DC power supply was connected to the graphite electrode and operated for 120-144 hrs. Electroremediation experiment have also been carried out at 5 and 15 volts. Voltage drop at different sections of the soil was monitored by using Multimeter along with current. To avoid hydraulic head driven flow, levels in the reservoirs were continuously adjusted to ensure that difference in electrolyte levels never exceeded 10 cm<sup>3</sup>.

### 3.2.5. Sampling

4 ml sample was taken to analyse kinetic of the process from -ve chamber and reservoir or +ve chamber and reservoir depends on in which direction chromium have come in. Samples were taken 5-6 times during the 5-6 days experiment, generally one time each days.

### 3.2.6. Extrusion

After 5-6 days experiment slurry material from the Pyrex tube was extruded by applying constant extruding force using a screw feeder mechanism. The pH profile of the soil was first measured using a universal pH paper.

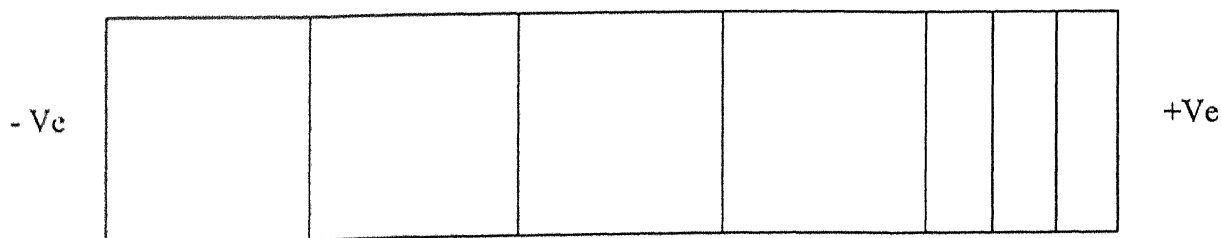


Fig. 3.2 7 sections of kaolin after extrusion.

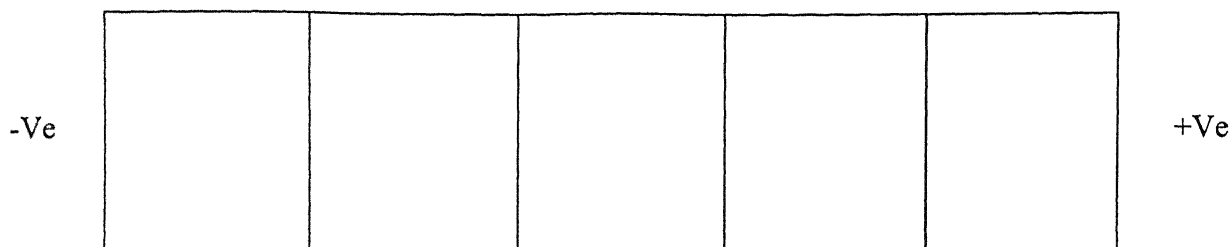


Fig. 3.3. 5 sections of kanpur soil after extrusion.

### 3.2.7. Cr(VI) Analysis

Each section of the soil was weighed and analysed for Cr(VI) and total chromium. Each section was first thoroughly mixed. To determine residual Cr(VI) in soil, some portion of samples from each soil section was mixed in conical flasks containing double distilled water and stirred for 2 hrs in a shaker. After 2 hrs shaking of the slurry material was centrifuged in a centrifugal instrument, at that time all soil particles settled down and soil particles free chromium solution was used for Cr(VI) analysis. Soil particles settling depends on the pH of the solution, in alkaline solution soil particles do not settle at that time 2-3 drops of concentrated  $H_2SO_4$  was added to settle down the soil particles. The resulting solution was analysed for Cr(VI) colorimetrically using US-EPA method. Measured quantity of Cr(VI) solution was taken in volumetric flask containing 2 pH solution to achieve desired Cr(VI) concentration and pH .05-2 PPM and 1-3 respectively in the volumetric solution. 2-3 drops of 1,5 diphenyl carbazide solution was added as indicator to develop violate colour for UV analysis. Diphenyl carbazide solution was produced by homogeneous mixing of 0.25 gm diphenyl carbazide in 50 ml acetone.

### 3.2.8. Moisture, Total Chromium and pH Analysis

Rest portion of slurry materials of all 7 sections were kept in oven at  $105^{\circ}C$  for 24-30 hrs to analyse moisture content. pH was measured by ASTM standards of 1:1 ratio. 4 gm of dry

soil was homogeneously mixed with 4 ml double distil water and corresponding pH was measured by digital pH meter MK VI. Total Cr(VI) analysis were done in 2 cases, case(1) Total Cr(VI) present in the chamber fluid and pore fluid in the slurry case(2) Total Cr(VI) present in the slurry materials.

Case(1) : Measured quantity of chromium leach liquor solution was taken in a kit and added 2 pH solution to achieve prerequisite range of chromium concentration 0.1-2 PPM and pH 1-3 respectively in the kit solution. Few ammonium per sulphate and sodium nitrate crystals were added in the kit solution to act as they catalyst and oxidiser respectively. Air tight kit was kept in a thermostat at 120<sup>0</sup> C for 1 hr. After that this solution was analysed as analyse Cr(VI) before.

Case(2) : Total Cr analysis was done by acid digesting 4 gm of dried sample from each sections in a mixture of concentrated nitric acid and sulphuric acid at 95°C for 2 hours. After acid digestion, the slurry was filtered in a 250 ml volumetric flux and then subjected to same process as mention in case(1).

### **3.2.9. Adsorption studies**

Adsorption studies were done by varying 2 parameter time and pH of the solution.

#### **3.2.9.1. Adsorption vs time :**

5 gm of pure soil was in a conical flask to which Lixiviant solution, DD water and H<sub>2</sub>SO<sub>4</sub> were added to achieve a prerequisite Cr(VI) of 25 ppm with a pH close to 2 in 50 ml solution. Seven weights of this experiments were made to analyse the weight percentage of Cr(VI) adsorbed with time. Cr(VI) analysis was done at 0<sup>th</sup>, 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup> and 6<sup>th</sup> days.

#### **3.2.9.2. Adsorption vs pH**

5 gm of pure soil was in a conical flask to which Lixiviant solution, DD water and H<sub>2</sub>SO<sub>4</sub> were added to achieve a prerequisite Cr(VI) of 25 ppm with a pH range 2-10 in 50 ml solution. Five

weights of this experiments were made at different pH to analyse the weight percentage of Cr(VI) adsorbed with pH for 3 days. Cr(VI) analysis was done at different pH close to 2, 4, 6, 8 and 10.

**Table. 1 Initial condition of the lixiviant-slurry.**

Soil	Applied Voltage	Wet Bulk Density	Dry Bulk Density	Void Ratio	Porosity	Degree of Saturation
kaolin	25	1.452497	1.092246	1.47197	59.54644	60.49911
kaolin	15	1.487965	1.11507	1.421372	58.7011	63.52435
kaolin	5	1.495194	1.121892	1.40665	58.44846	63.86874
kanpur	25	1.899039	1.651213	0.635162	38.84397	62.9402
kanpur	15	1.83108	1.587154	0.701158	41.21652	41.5202
kanpur	5	1.843007	1.601242	0.686191	40.69473	54.03897

# CHAPTER IV

## RESULTS AND DISCUSSION

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### Introduction

The mode of transport mechanism, the effect of voltage on rate controlling mechanism, unremediated chromium, effect of voltage on removal efficiency and energy efficiency will be described.

### 4.1. Kaolin

#### 4.1.1. Predominant Transport Mechanism

The movement of water soluble Cr (VI) towards the cathode or the anode depends on both electroosmosis and electromigration. Because Cr (VI) exists as anions ( $\text{HCrO}_4^-$  or  $\text{Cr}_2\text{O}_7^{2-}$ ) in aqueous medium, it moves toward the anode by electromigration. As the clay particles are negatively charged, electroosmosis will transport Cr (VI) towards the cathode chamber. Consequently, for Cr(VI) removal, there is a tug-of-war between electroosmosis and electromigration. Accumulation of chromium in the anode chamber for experiments with kaolin shows that electromigration is the predominant driving force for the transport of Cr(VI).

### 4.1.2. Rate Controlling Mechanism

Fig. 4.1 shows that chromium is removed at a constant rate till ~20 hours, till when approximately 20 % of total Cr(VI) is removed from kaolin. Thereafter, there is a drastic reduction in the chromium removal rate. After 124 hours only 36.6 % total chromium, is removed from kaolin. In case of 15 volts kaolin experiment, chromium is removed at a constant rate till ~40 hours as shown in Fig. 4.2.

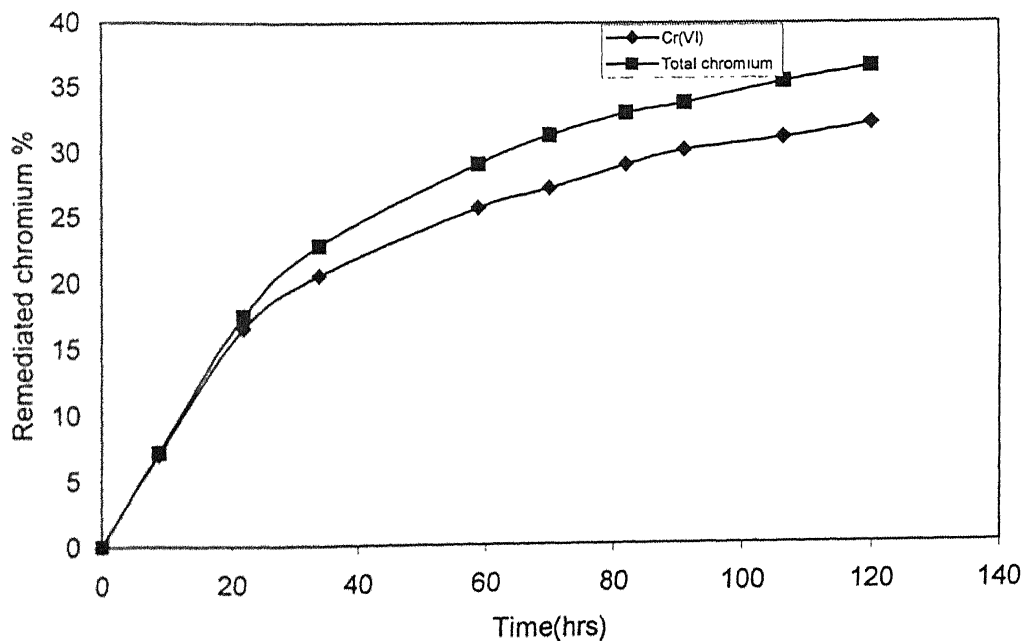


Fig. 4.1. Electroremediation of chromium from kaolin as a function of time (V = 25 volts)

In an electrolytic cell, flow of current in the electrolyte is represented by the migrating flux of all ions. Thus variation of current with time, shown in Figs. 4.3 and 4.4 could shed light on the kinetics of chromium removal. A comparison of Figs. 4.1 and 4.2 show that the times corresponding to the “peak” and “plateau” in the current and chromium removal rate are coincident. Unfortunately, Figs. 4.3 and 4.4 does not “reveal” the rate controlling mechanism, answer for which is provided by the potential distribution plot, depicted in Figs. 4.5 and 4.6.

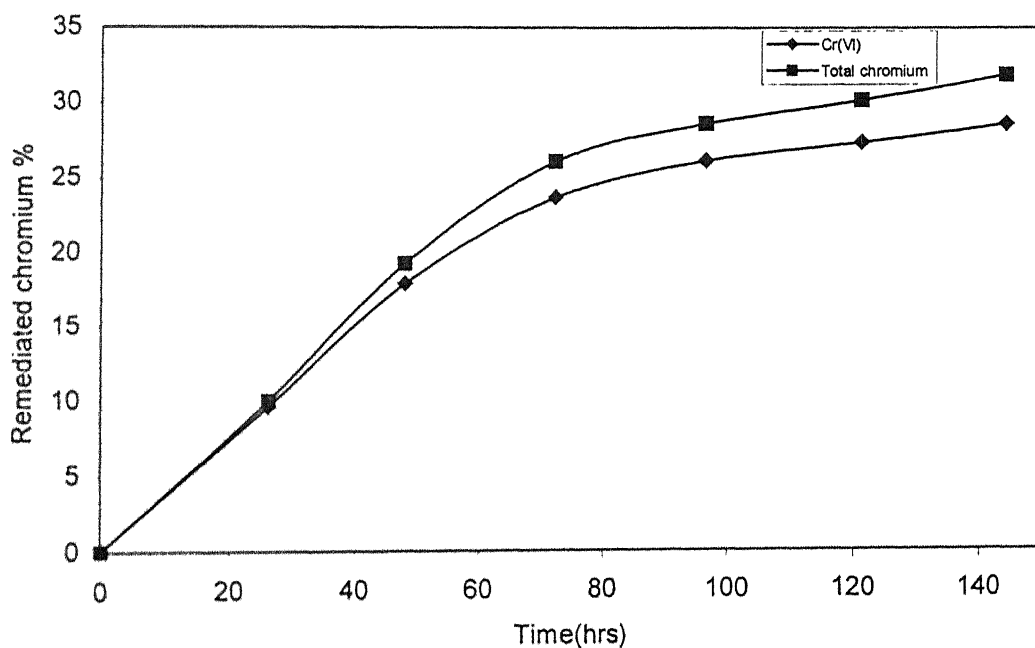


Fig. 4.2. Electroremediation of chromium from kaolin as a function of time ( $V = 15$  volts)

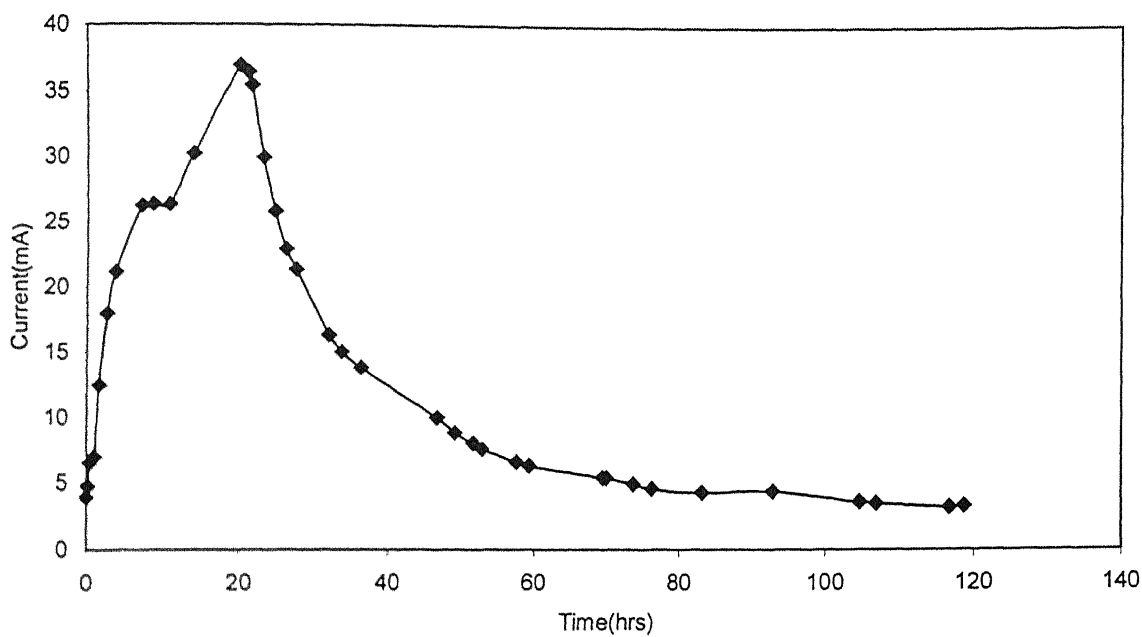


Fig. 4.3. Variation of current as a function of time of kaolin ( $V = 25$  volts)

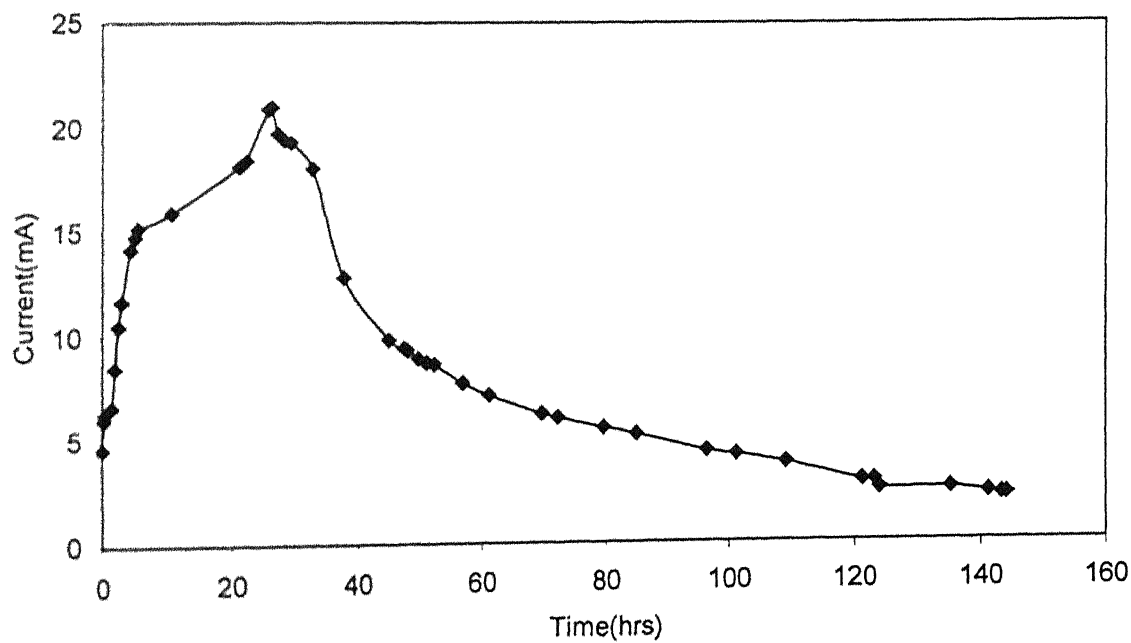


Fig. 4.4. Variation of current as a function of time of kaolin ( $V = 15$  volts)

Figs. 4.5 and 4.6 show that potential drop in both the anode cathode compartments falls sharply in the initial stages of the experiment and is therefore responsible for the initial increase in cell current from 3mA to 37mA and 2.5 to 21mA respectively. The initial decrease in potential is due to the (i) generation of  $H^+$  and  $OH^-$  in the electrode chambers and (ii) increase in kaolin water content due to "electroosmotic flow". It is further seen in Figs. 4.5 and 4.6 that the maximum current coincides with the sharp increase in voltage drop in section 1, which is immediately adjacent to the cathode. In fact, after 40 hours, the voltage drop in section 1 constitutes more than 65 and 55 % respectively of the applied voltage. The unusually high voltage drop in section 1 reduces the effective driving force for both electromigration and electroosmosis, resulting in a drastic reduction in the chromium removal rate. Electroosmotic flow rate, which is proportional to the potential gradient, drastically falls down after 40 hours for 25 volts and 15 volts experiments as shown in Fig. 4.7. This phenomenon can be attributed to the high potential gradient in section 1 compared to the other sections. The pH profile in kaolin is also responsible for the reduction of electroosmotic flow. As shown in the following paragraph, the pH of kaolin gradually attains a pH of 2, thereby reducing the magnitude of zeta potential. It may be pointed out that electroosmotic flow is also proportional to zeta potential.

Hamed et al. [5] attributed the high voltage drop near the cathode to the depletion of ion carriers due to acid base neutralization. Fig. 4.8 shows that more than 90% of the entire soil section becomes acidic at the end of electroremediation. pH measurements also showed that kaolin close to the cathodic end was basic. In fact, experiments conducted by Sanjay et. al. [27] at 25 volts show that the basic and acid fronts meet after approximately 20 hours, which happens to be the time after which the voltage drop in section 1 starts increasing. Consequently, acid-base neutralization appears to be the rate-controlling step in the electrochemical cleaning of chromium-contaminated kaolin.

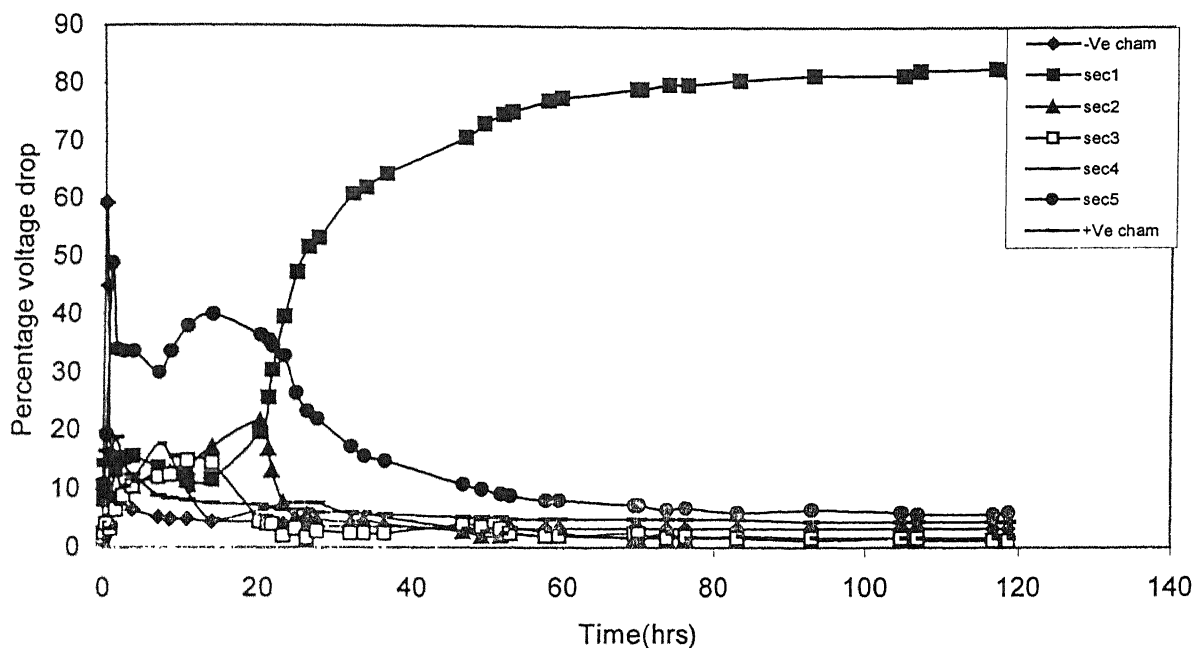


Fig. 4.5. Percentage voltage drop at different sections of kaolin as a function of time (V = 25 volts).

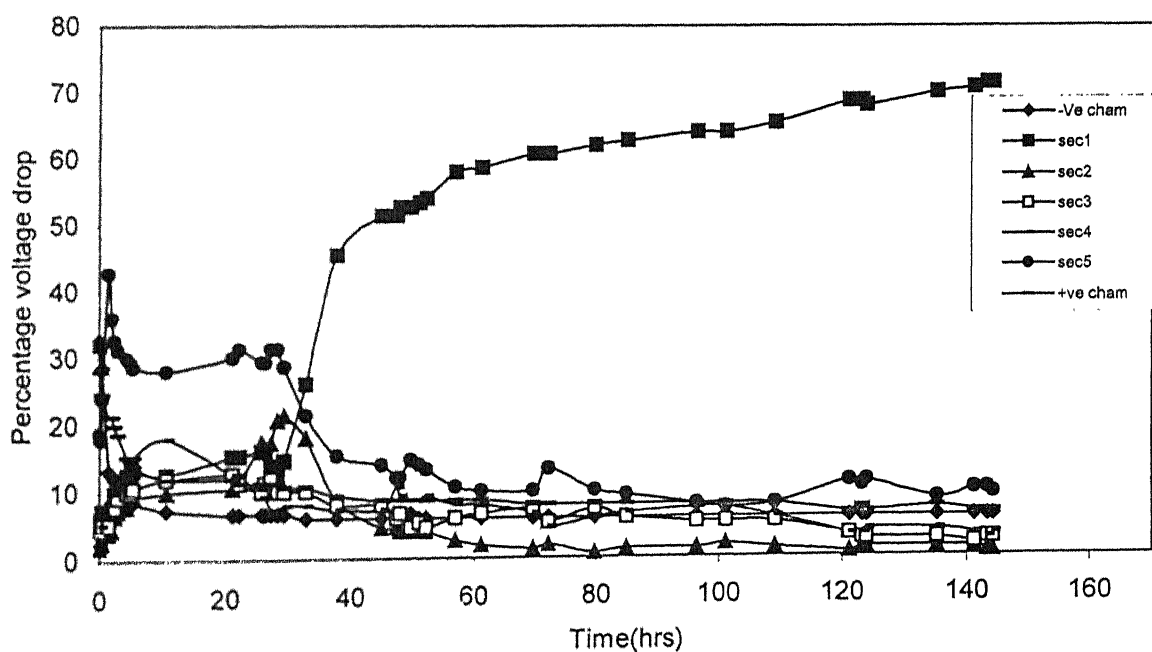
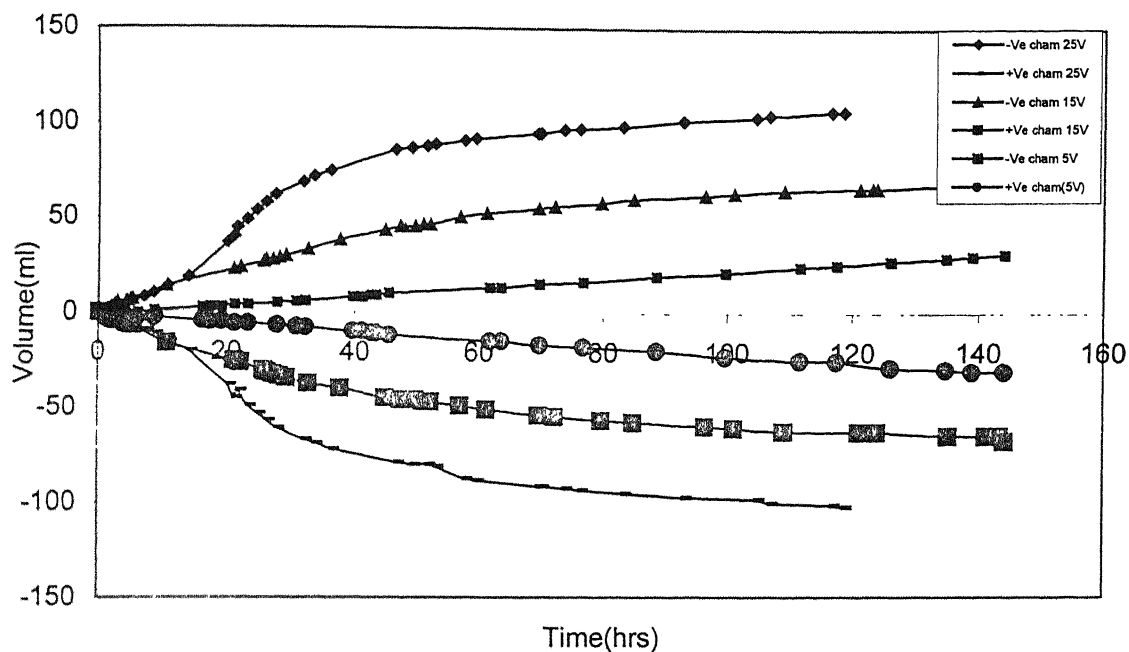


Fig. 4.6. Percentage voltage drop at different sections of kaolin as a function of time (V = 15 volts)



### Equation of electroosmotic flow at different voltage condition of kaolin

25 volts:  $y = -1E-07x^5 + 3E-05x^4 - 0.0032x^3 + 0.1217x^2 + 0.6435x - 1.2211$  [ $R^2=0.9968$ ]

15 volts:  $y = -2E-07x^4 - 0.0032x^3 + 0.1217x^2 + 0.6435x - 1.2211$  [ $R^2=0.9968$ ]

5 volts:  $y = 0.219x - 0.7027$  [ $R^2 = 0.9986$ ]

y is volume (ml) of electroosmotic flow in -ve chamber.  
x is time (hrs)

Fig. 4.7. Electroosmosis as a function of time of kaolin at different applied voltage.

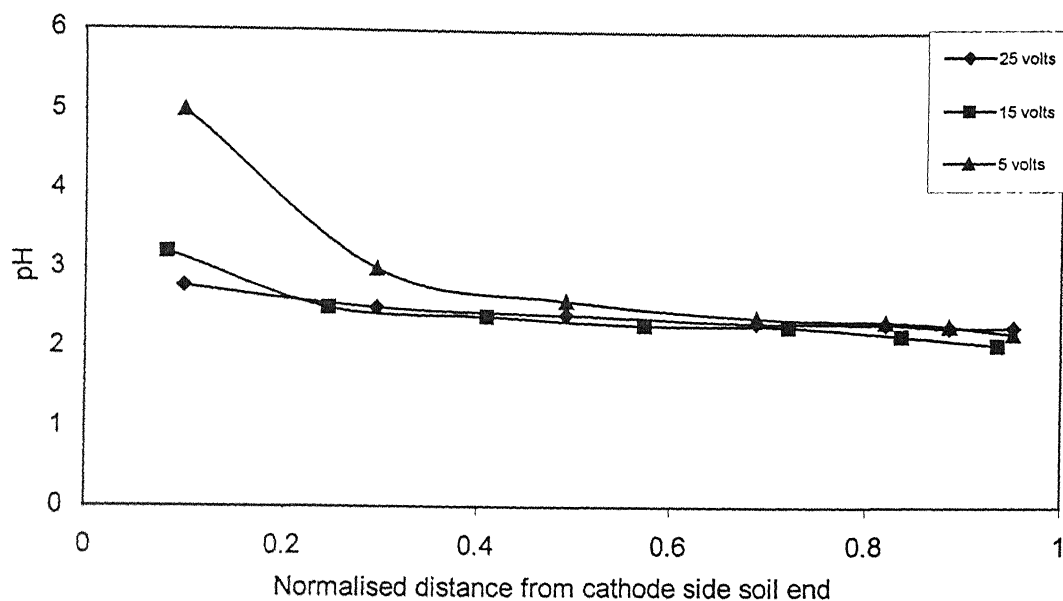


Fig. 4.8. pH distribution profile in kaolin after the end of experiment.

Unlike the 25 and 15 V experiments, experiments at 5 volts showed a constant Cr(VI) remediation rate (see Fig. 4.9). Fig. 4.10 shows that the high potential drop in section 1 in the higher voltage experiments was not evident at 5 volts, a phenomenon that can be attributed to lower migration velocity of  $H^+$  towards the cathodic end of kaolin. Consequently, a comparison of Fig. 4.11 with Figs. 4.3 and 4.4 shows that the current does not decrease drastically in the 5 volt experiment.

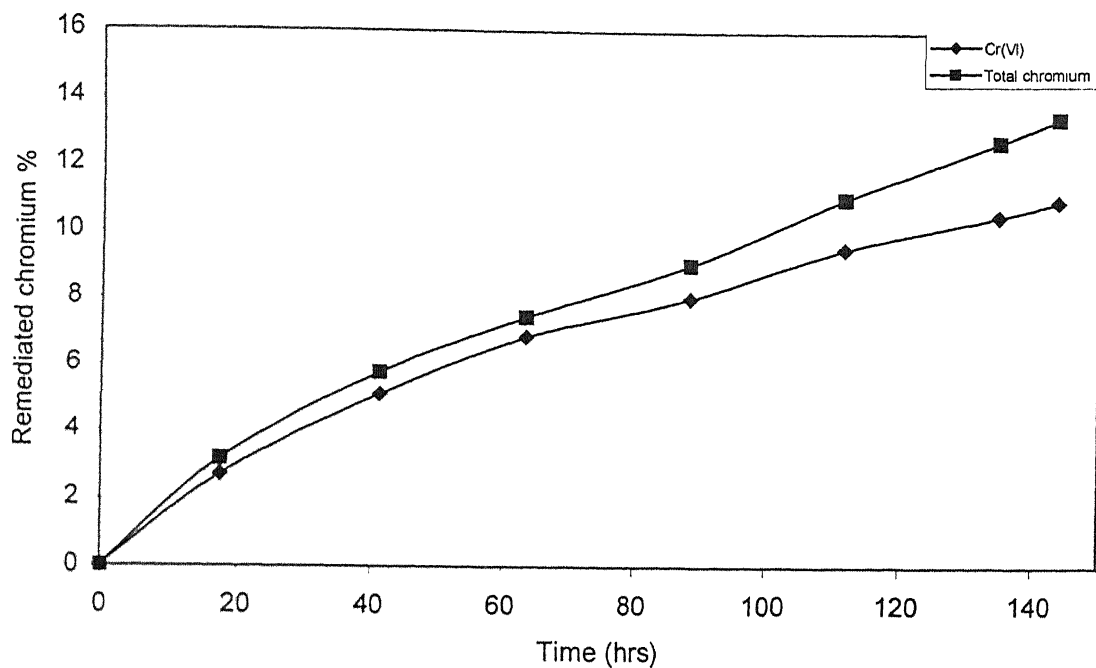


Fig. 4.9. Electroremediation of chromium from kaolin as a function of time ( $V = 5$  volts).

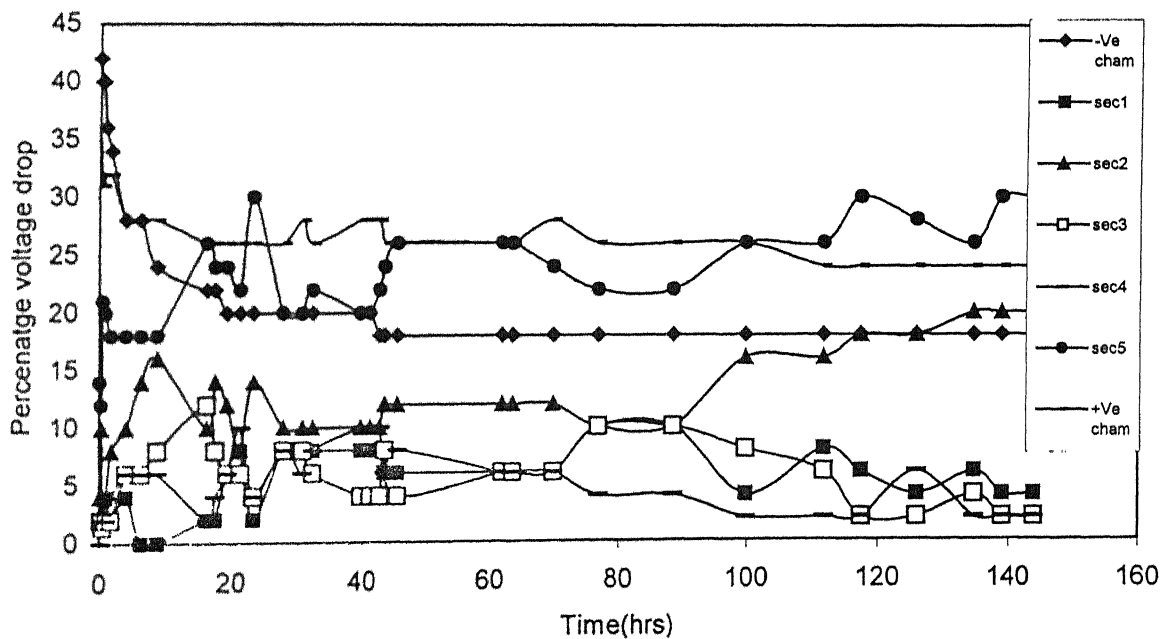


Fig. 4.10. Percentage voltage drop at different sections of kaolin as a function of time ( $V = 5$  volts).

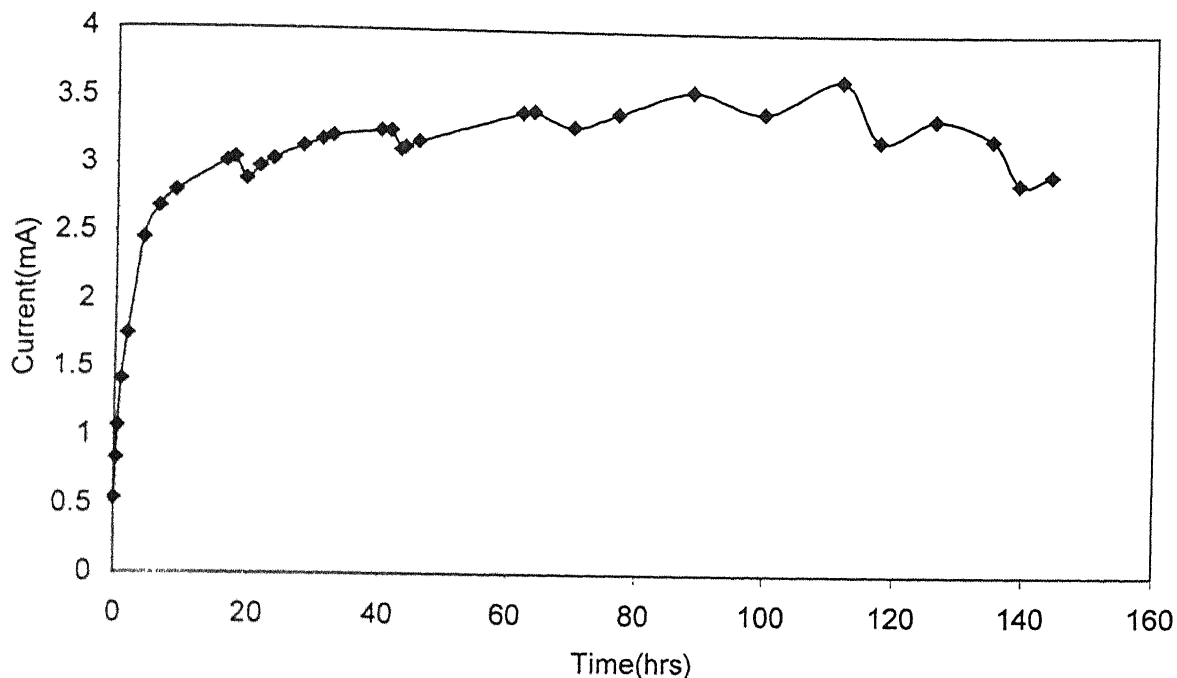


Fig. 4.11. Variation of current as a function of time of kaolin ( $V = 5$  volts)

### 4.1.3. Unremediated Chromium

Cr(VI) concentration in kaolin at the end of electroremediation is shown in Figs. 4.12, 4.13 and 4.14 for 25, 15 and 5 volts experiment respectively. Figs. 4.12 - 4.14 depict that the unremediated Cr(VI) accumulates in the center of kaolin. This phenomenon, in the 15 volts and 25 volts experiments, can be attributed to the relatively small voltage drop, the driving force for electromigration, in sections away from the cathodic end of kaolin (see Figs 4.5 and 4.6). In essence, Cr(VI) starts migrating towards the anode “readily” until the time when the voltage drop in section 1 starts increasing. After the voltage drop in section 1 reaches its maximum values, the axial concentrations of Cr(VI) remains more or less constant with time, as is evident from

Figs. 4.1 and 4.2. In the 5 volts experiment, low Cr(VI) concentrations near the anode can be attributed to the high potential drops in sections 4 and 5, adjacent to the anodic end of kaolin.

A mass balance of chromium showed that 4%, 4.1% and 3.2% chromium was unaccounted for. Total chromium analysis of kaolin showed that most of the missing chromium was present as “strongly adsorbed” species. Table 4.1 shows the details of the chromium mass balance. The unaccounted chromium may have been adsorbed on the anode [10] as shown in Table. 4.1 for 15 and 25 volts kaolin experiment. Adsorption in kaolin is high at acidic pH as shown in the Fig. 4.14. The adsorption of chromium can be attributed to the acid conditions existing in kaolin, as is evident from Fig. 4.8.

**Table 4.1 Mass Balance of Kaolin**

Soil	Volts	Days	Remediated Chromium (Wt. %)	Unremediated Chromium (Wt. %)	Adsorbed Chromium (Wt. %)	Unaccounted Chromium (Wt. %)
Kaolin	25	5	36.6	48.92	10.48	4
Kaolin	15	6	31.82	51.85	12.23	4.1
Kaolin	5	6	15.32	74.47	7.006	3.2

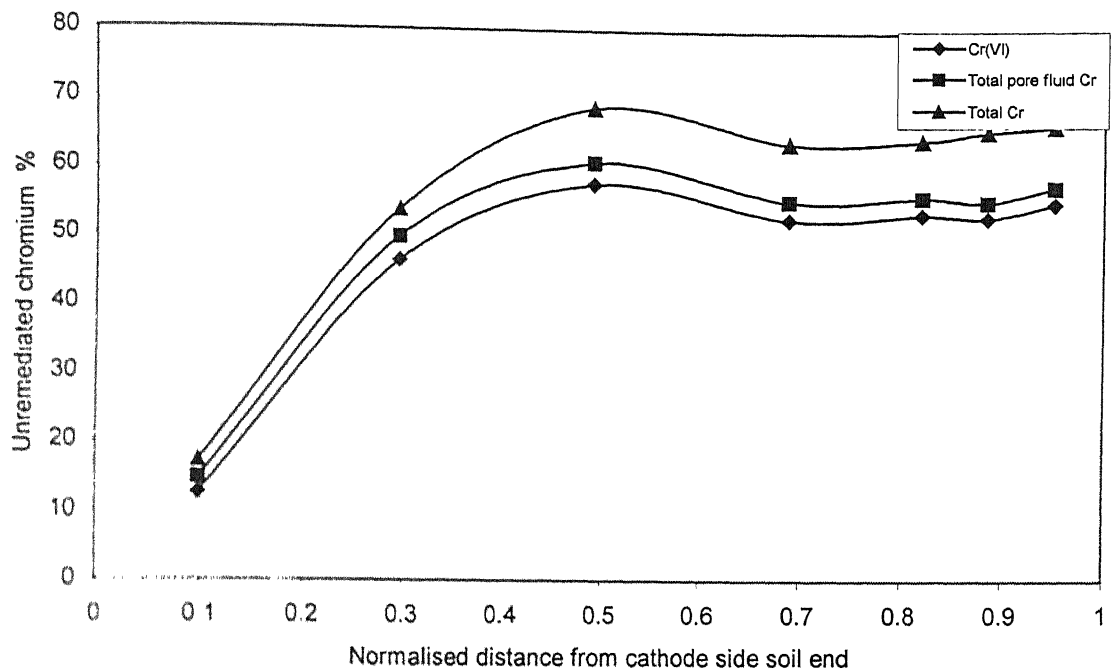


Fig. 4.12. Unmediated chromium distribution in kaolin ( $V = 25$  volts)

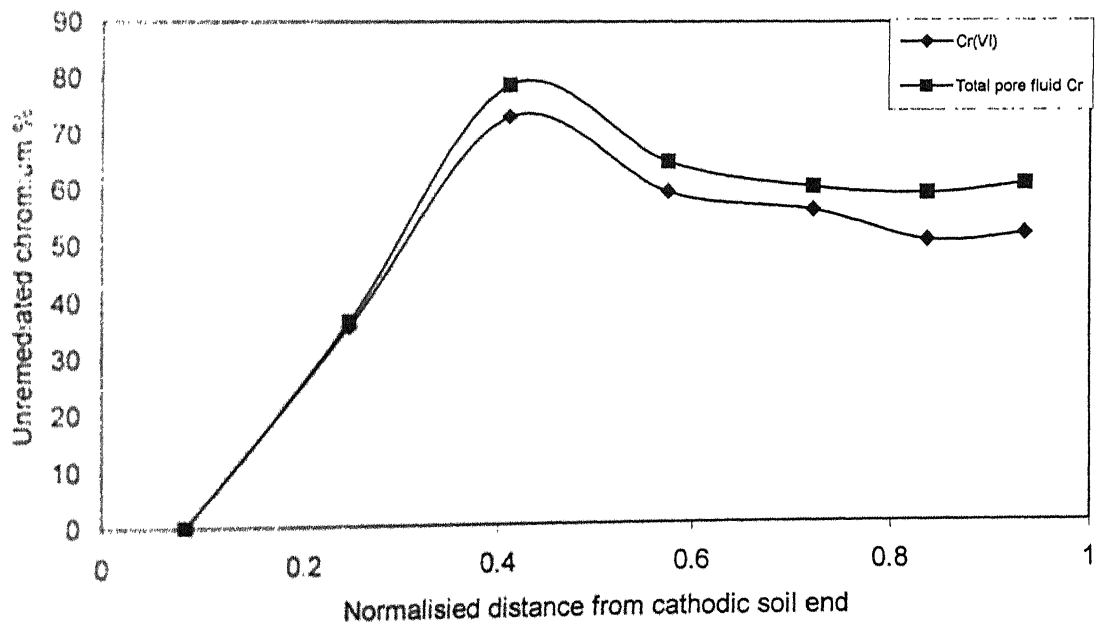


Fig. 4.13. Unmediated chromium distribution in kaolin ( $V = 15$  volts)

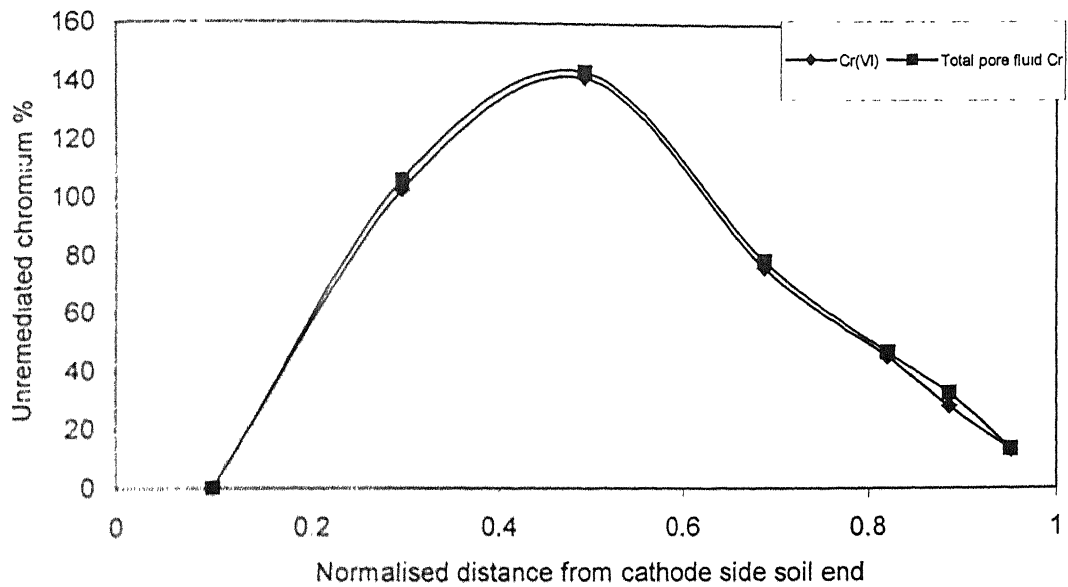
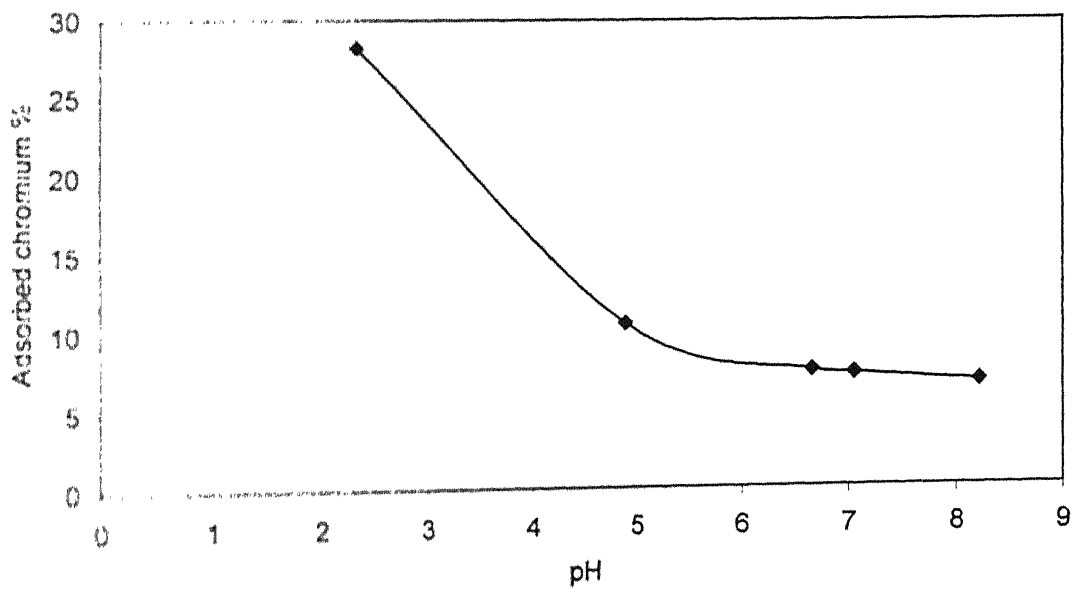


Fig. 4.14. Unremediated chromium distribution in kaolin (V = 5 volts).



**Equation of adsorbed Cr(VI) as a function of pH**

$$y = -0.1409 x^3 + 3.149 x^2 - 23.855 x + 68.35 \quad [R^2 = 1]$$

Fig. 4.15. Adsorption of chromium in kaolin at different pH for 3 days.

#### 4.1.4. Effect of Voltage

The effect of voltage on specific power consumption is described in the following paragraph. Specific power consumption is defined as:

Specific power consumption = Total watt-hrs consumed per day/(% chromium removed)

Fig. 4.16 is a plot of power consumption per unit percent chromium removed from kaolin, a measure of energy consumption versus applied voltage. This also shows that increase in applied potential translates into higher power consumption or lower energy efficiency.

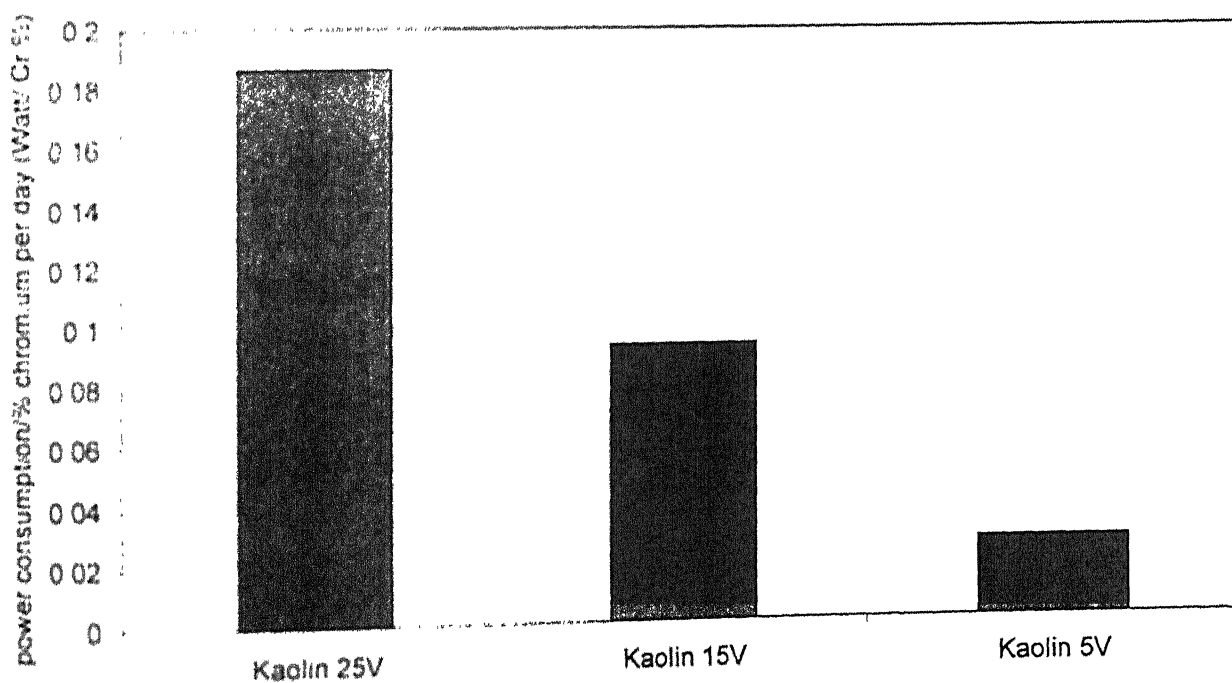


Fig. 4.16. Specific power consumption at different applied voltage of kaolin.

#### **4.1.4.1. Optimum Voltage:**

From removal and energy efficiency point of view we are getting two different aspects, application of constant voltage for electroremediation is depend on the two factors. If removal efficiency factor is more important over energy consumption, then higher voltage experiment is better. Reverse will be true, if energy consumption for per mg Cr(VI) removal is the main factor.

## **4.2. Kanpur Soil**

### **4.2.1 Predominant Transport Mechanism**

Accumulation of chromium in the cathode chamber for experiments with Kanpur soil shows that electroosmotic flux is the predominant driving force for the transport of Cr(VI).

### **4.2.2. Rate Controlling Mechanism**

Fig. 4.17 is a plot of chromium remediation from Kanpur soil as a function of time at 25 volts. At 25 volts more than 80% chromium is removed in 80 hours, after which its removal ceases. This is in sharp contrast to experiments in kaolin where only 36.5% chromium is removed at 25 volts, clearly pointing to the importance of the nature of the soil in determining electroremediation efficiency.

The difference between kaolin and Kanpur soil and their effect on electroremediation efficiency is amply demonstrated by a comparison of Fig. 4.5 and 4.18. Unlike kaolin, the voltage drop in section 5, immediately adjacent to the anode, rises immediately and constitutes about 75% of the applied voltage. After approximately seventy hours, the voltage drop in section 5 starts decreasing with a corresponding increase in the voltage drop of section 4. It may be pointed out that in kaolin, the voltage drop in section 1, adjacent to the cathode, consumes more than 80% of the applied potential after approximately 40 hours (see Fig. 4.5). The difference in the evolution of voltage drop in kaolin and Kanpur soil can be attributed to the fact that while the former is

weakly acidic ( $\text{pH} = 5.5$ ), the latter is basic ( $\text{pH} = 10$ ). Moreover, Kanpur soil acts as a strong basic buffer. Consequently, the motion of the acid front is slowed down considerably and acid-base neutralization takes place in section 5. As the acid front moves with time, so does the position of the acid-base neutralization front. Hence the location of the predominant voltage drop is expected to shift gradually first within section 5 itself, then to section 4, to section 3 and so on. Considering the above-mentioned observations, the most probable mechanism of chromium removal in Kanpur soil is:

- a) The high voltage drop in section 5 acts as an electroosmotic pump, pumping the electrolyte, along with chromium, towards the cathode.
- b) Most of the soil remains basic during the course of the experiment, as will be shown later, leading to a nearly invariant zeta potential, which the electroosmotic transport of electrolyte.

It has already been pointed out that electroosmotic flow is directly proportional to both the voltage gradient and the zeta potential. A negative zeta potential, obtained under basic pH, drives electroosmotic flow towards the cathode.

Fig. 4.19 shows that chromium is continuously removed from the soil, with approximately 35% remediation in 6 days. The evolution of voltage profile is similar to that observed in the 25 V experiment, as shown by a comparison of Figs. 4.18 and 4.20. It is also interesting to note that at 5 volts (Fig. 4.21), the total chromium removed is nearly the same as that obtained in the 15 volts experiment. The corresponding voltage drop plot is shown in Fig. 4.22 where it is seen that the voltage drop in section 5 remains constant at 50% of the applied voltage throughout the duration of the experiment. The fact that the voltage drop in section 4 continues to remain low can be attributed to the relatively slower motion of the acid front compared to the 15 and 25 volts experiments. Another interesting observation from Fig. 4.22 is the relatively high voltage drops in the anode and cathode chambers, which is due to the lower rate of generation of  $\text{H}^+$  and  $\text{OH}^-$  respectively at 5 volts. It is also seen at all the three voltages that the voltage drop in the anode chamber is greater than the voltage drop in the cathode chamber.

The kinetic plots (Figs. 4.17, 4.19 and 4.21) also show that there is a gestation period before the chromium appears in the cathode chamber. The gestation period correlates very well with electroosmotic flow shown in Fig. 4.23. Fig. 4.23 shows that the volume of the cathode reservoir does not increase immediately after the commencement of the experiment as in kaolin. During the gestation period, electroosmotic flow actually fills up the pores within the soil, as is evident by the increase in the degree of saturation of the soil from an average of about 55% (please see Table 3.1) to approximately 70-90%. Lower gestation periods at higher voltage can be attributed to higher electroosmotic flow.

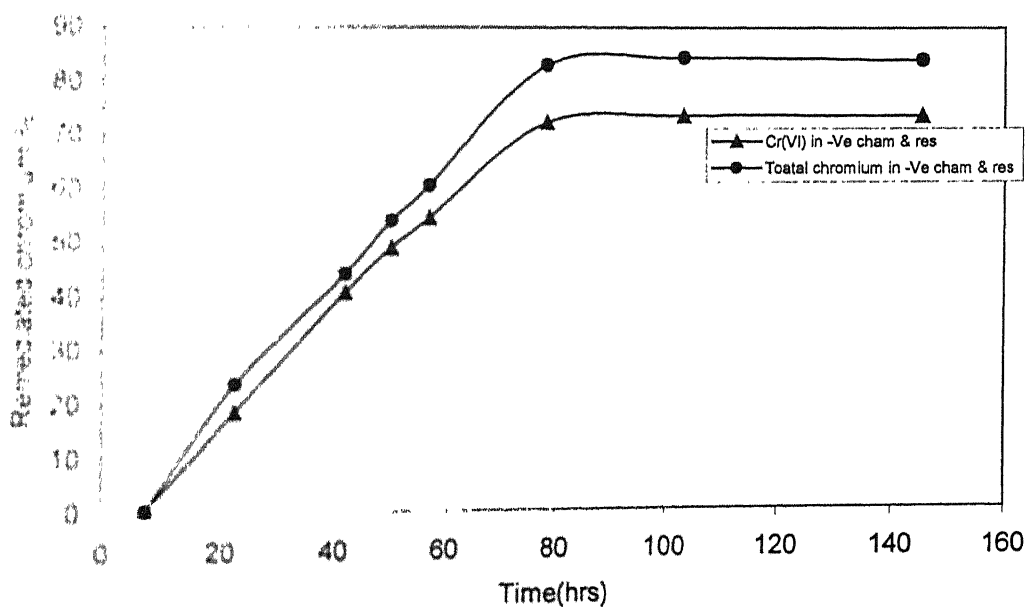


Fig. 4.17. Electroremediation of chromium from Kanpur soil as a function of time (V = 25 volts).

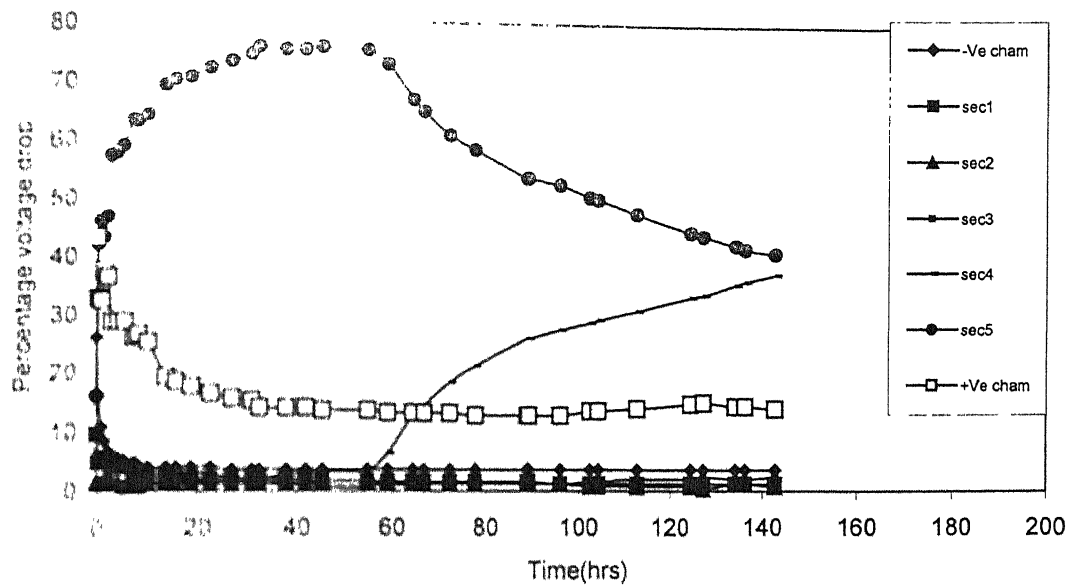


Fig. 4.18 Percentage voltage drop at different sections of Kanpur soil as a function of time ( $V = 25$  volts).

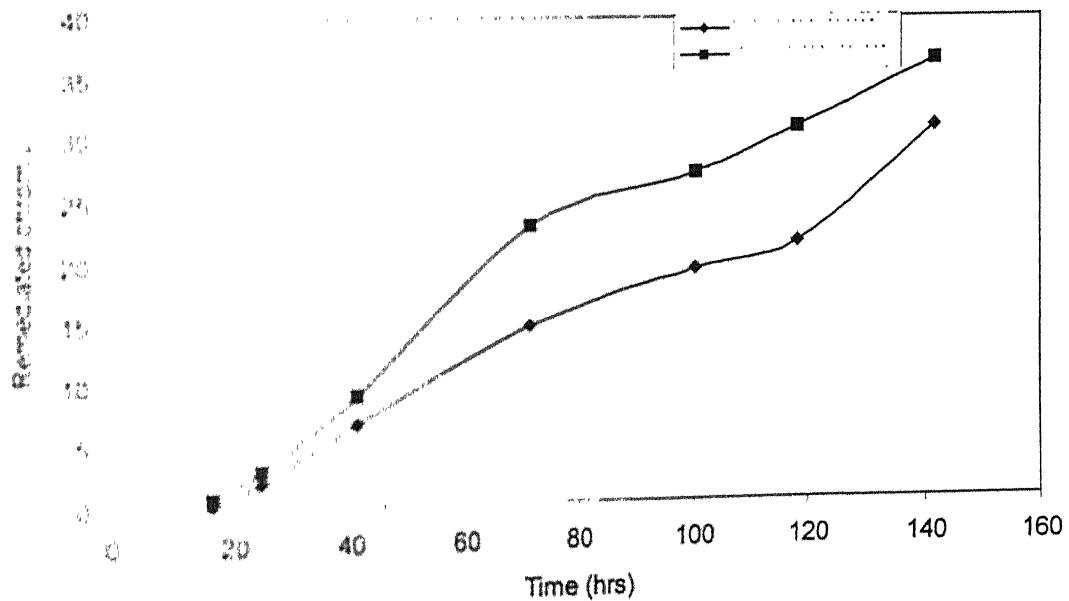


Fig. 4.19 Electroremediation of chromium from Kanpur soil as a function of time ( $V = 15$  volts).

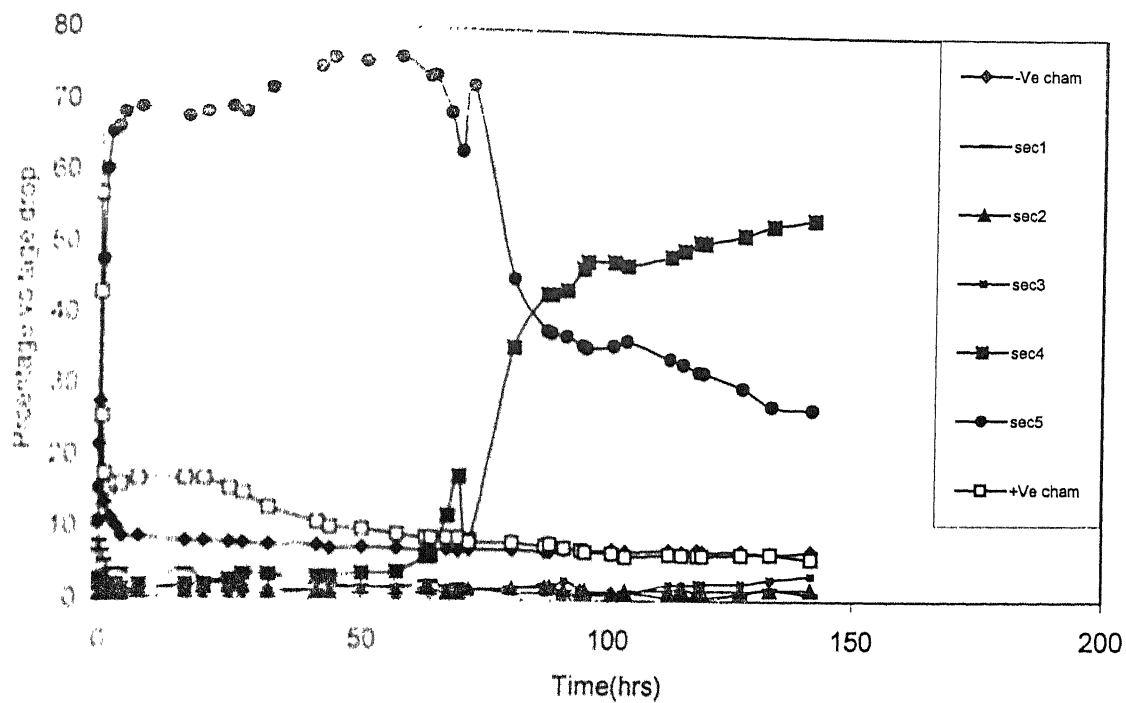


Fig. 4.20. Percentage voltage drop at different sections of Kanpur soil as a function of time ( $V = 18$  volts).

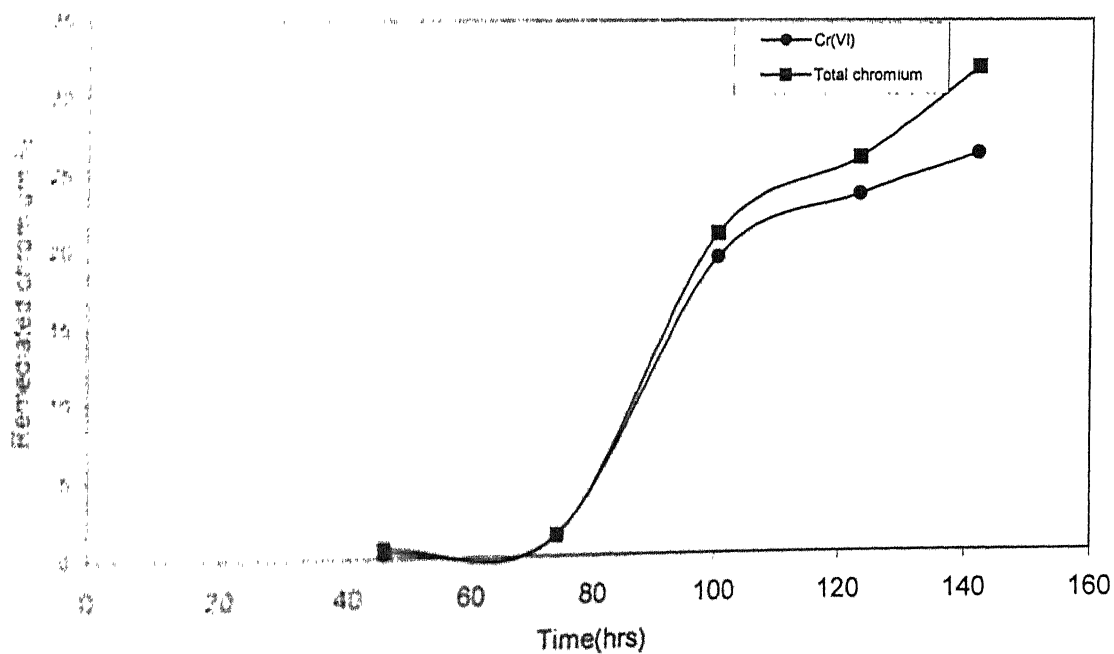


Fig. 4.21. Electroremediation of chromium from Kanpur soil as a function of time ( $V = 5$  volts)

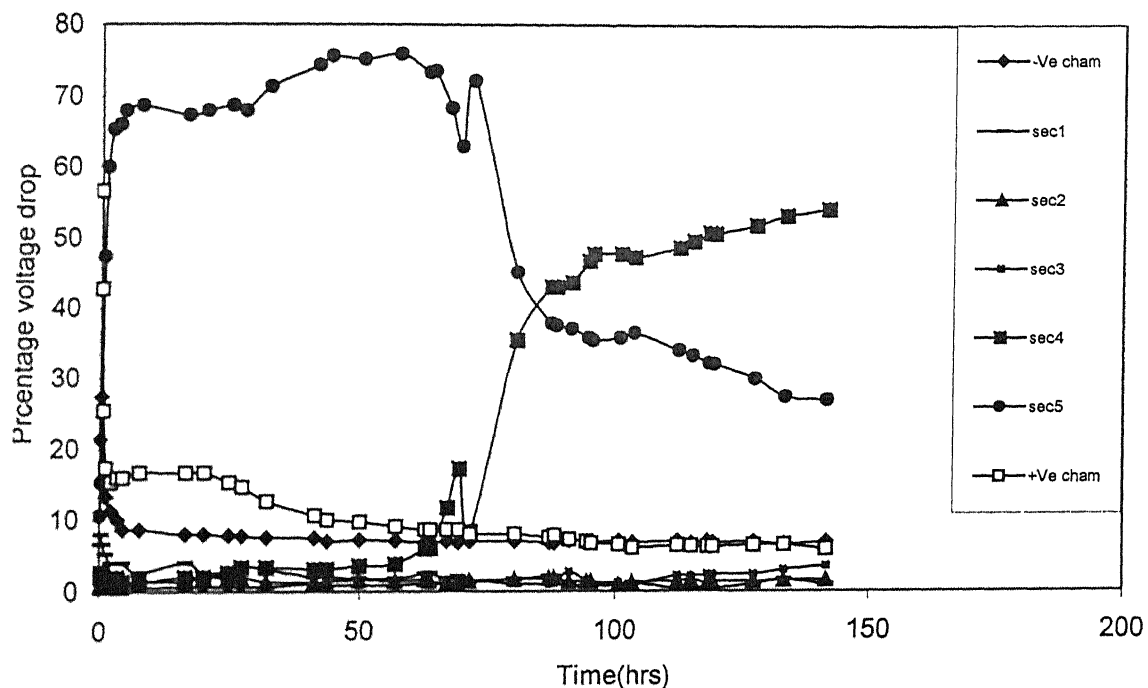


Fig. 4.20. Percentage voltage drop at different sections of Kanpur soil as a function of time ( $V = 15$  volts).

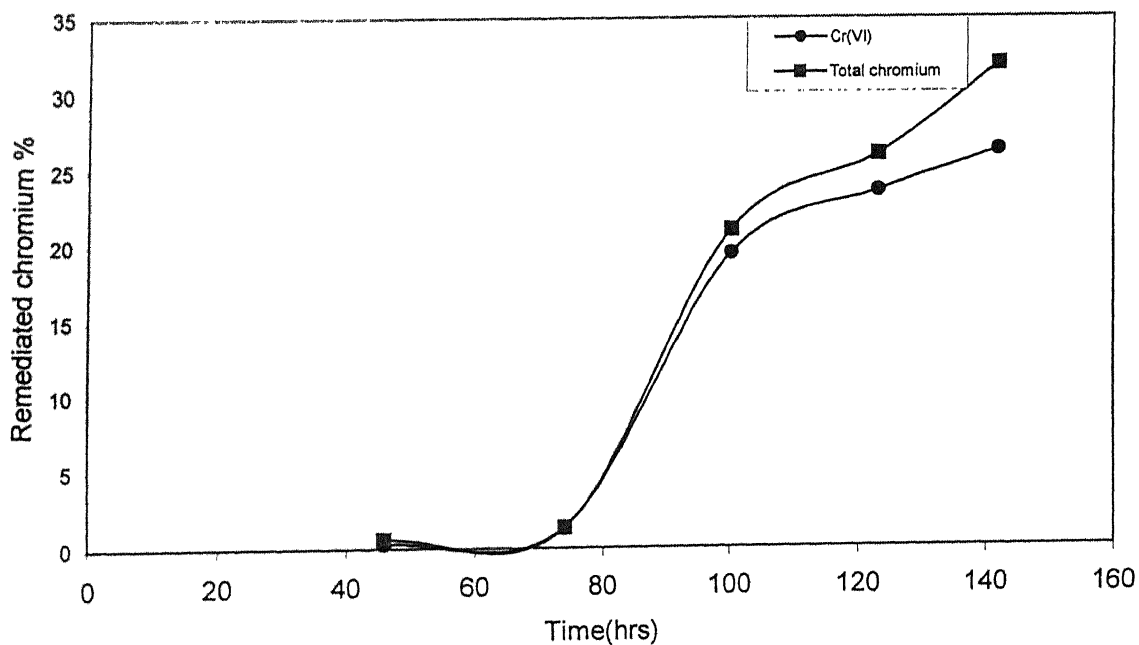


Fig. 4.21. Electroremediation of chromium from Kanpur soil as a function of time ( $V = 5$  volts)

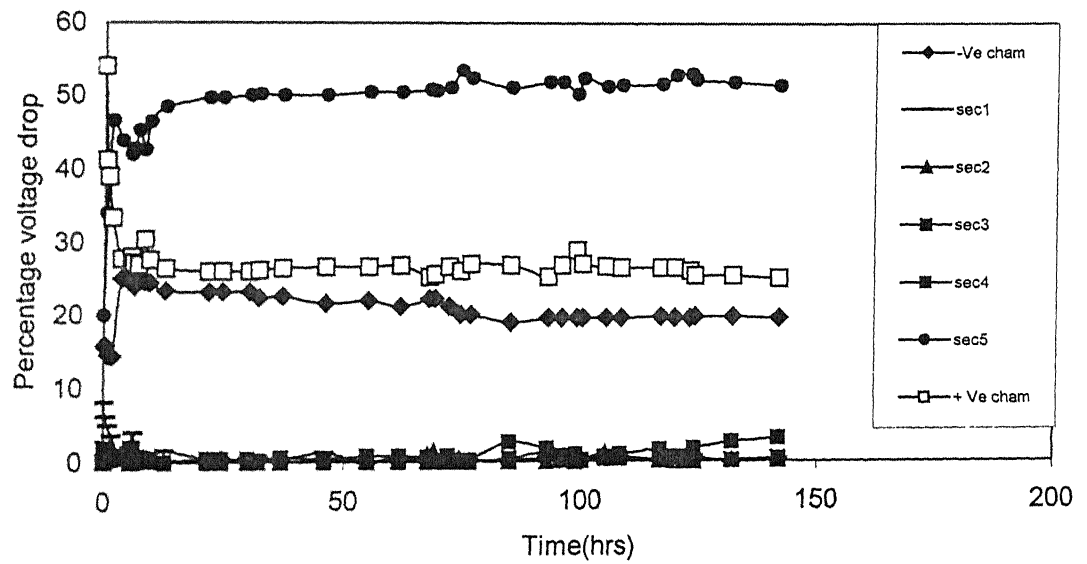
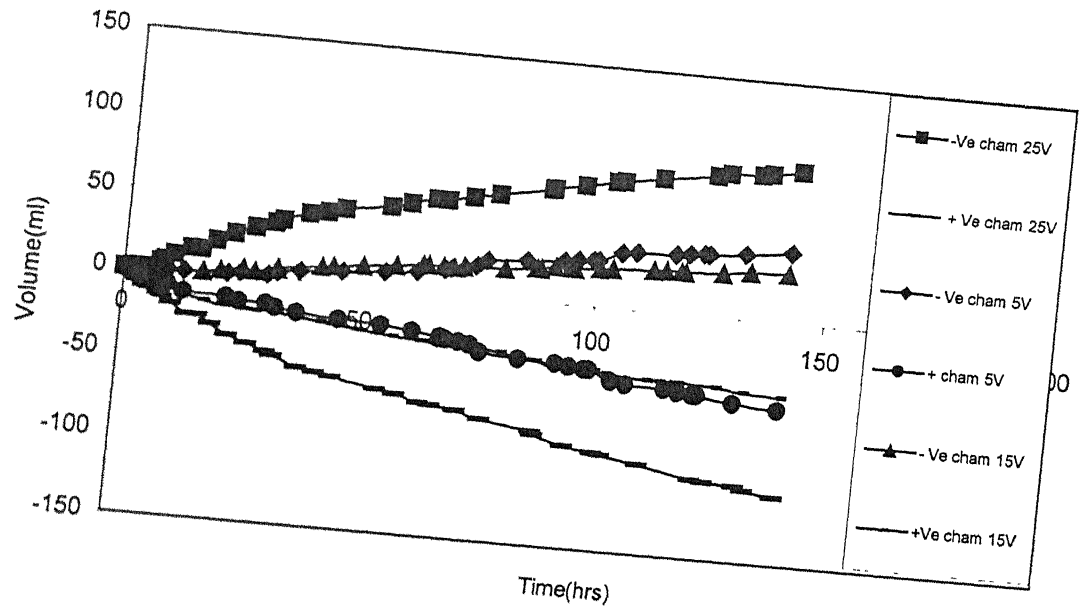


Fig. 4.22. Percentage voltage drop at different sections of Kanpur soil as a function of time ( $V = 5$  volts).



### Equation of electroosmotic flow at different voltage condition of Kanpur soil

25 volts:  $y = 0.7035x + 5.5608$  [ $R^2=0.9646$ ]

15 volts:  $y = 0.3317x - 3.6754$  [ $R^2=0.9720$ ]

5 volts:  $y = 0.2383x - 0.3384$  [ $R^2 = 0.9851$ ]

y is volume (ml) of electroosmotic flow in -ve chamber.

x is time (hrs)

Fig. 4.23. Electroosmosis as a function of time of knur soil at different applied potential.

### 4.2.3. Unremediated Chromium

Fig. 4.24 depicts that no unremediated chromium presents in the pore fluid solution at 25 volts. However, total chromium analysis shows that 10 % chromium is present in the soil as “strongly adsorbed” species. Fig. 4.25 shows that chromium adsorbs significantly in Kanpur soil only under highly acidic conditions, as in kaolin. Fig. 4.26 shows that majority of the soil section remains basic. Hence the extent of adsorption is expected to be small in Kanpur soil. The extent of unremediated chromium in all the three experiment is summarized in Table. 4.2

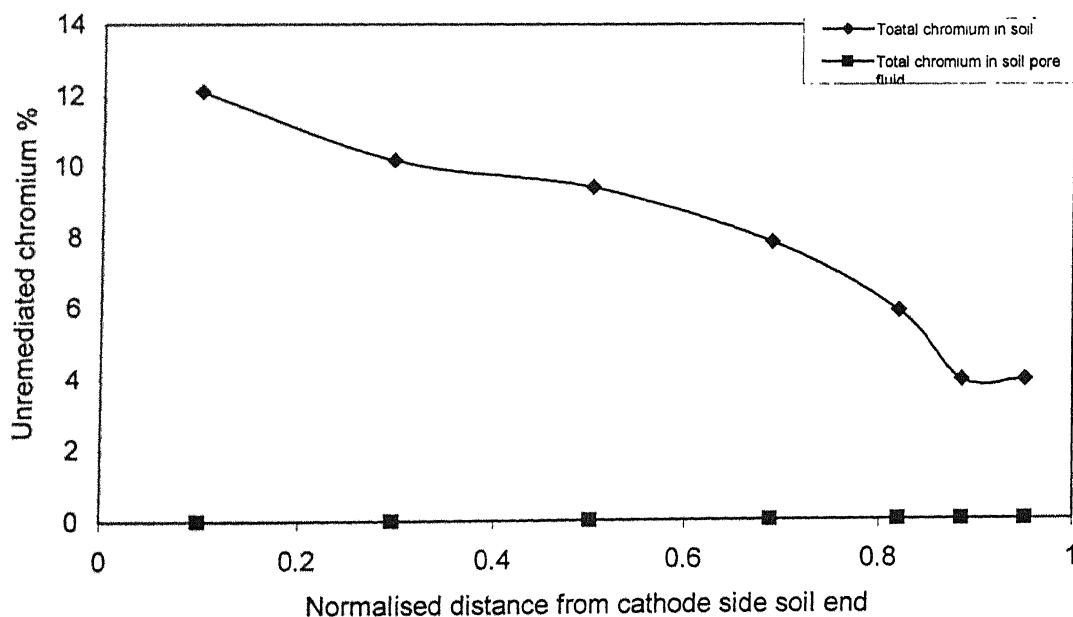
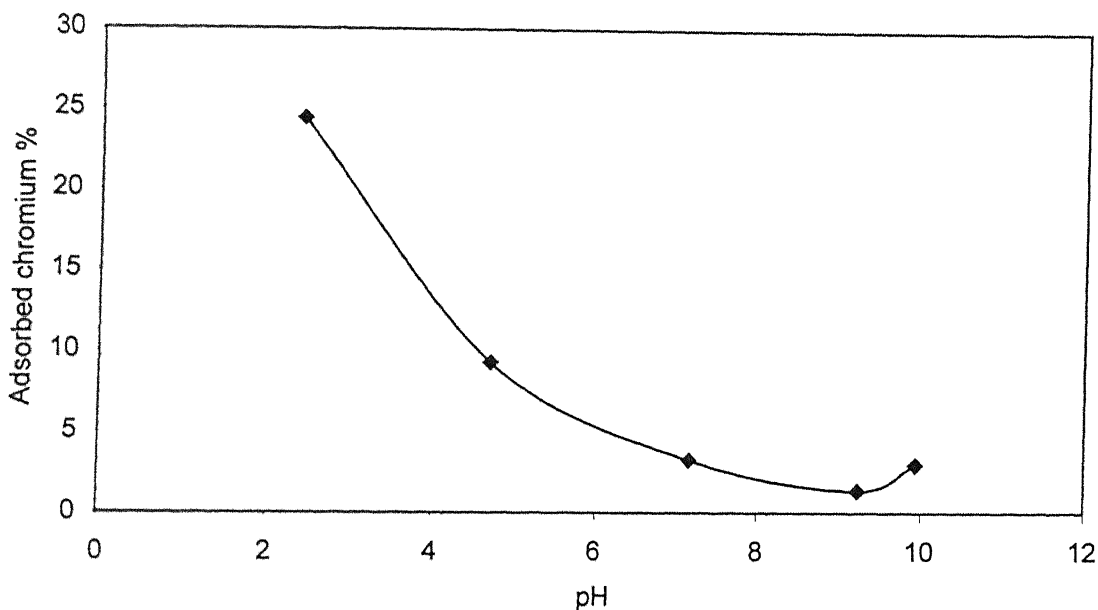


Fig. 4.24. Unremediated chromium distribution in Kanpur soil (V = 25 volts)



#### Equation of adsorbed Cr(VI) % as a function of pH

$$Y = 0.6277x^2 - 10.554x + 45.771 \quad [R^2 = 0.9952]$$

Fig. 4.25. Adsorbed chromium in Kanpur soil at different pH for 3 days.

pH profile after end of experiment of Kanpur soil at different applied voltage is shown in Fig. 4.26 after end of the experiments anode side soil is acidic and cathode side soil is basic in nature. Basic nature of Kanpur soil is maximum at 5 volts experiment. Fig. 4.27 shows that unremediated pore fluid chromium concentration is high at the cathode side soil end. This is happened due to uniform electroosmotic flow as shown in Fig. 4.23 and low migrating flux as shown in Fig. 4.28. Some peculiarity is happened of unremediated chromium in the pore fluid of 15 volts Kanpur soil experiment as shown in Fig. 4.29 due to the high migrating flux as shown in Fig. 4.30 and uniform electroosmotic flow as shown in Fig. 4.23. This is attributed by highly compacted slurry material.

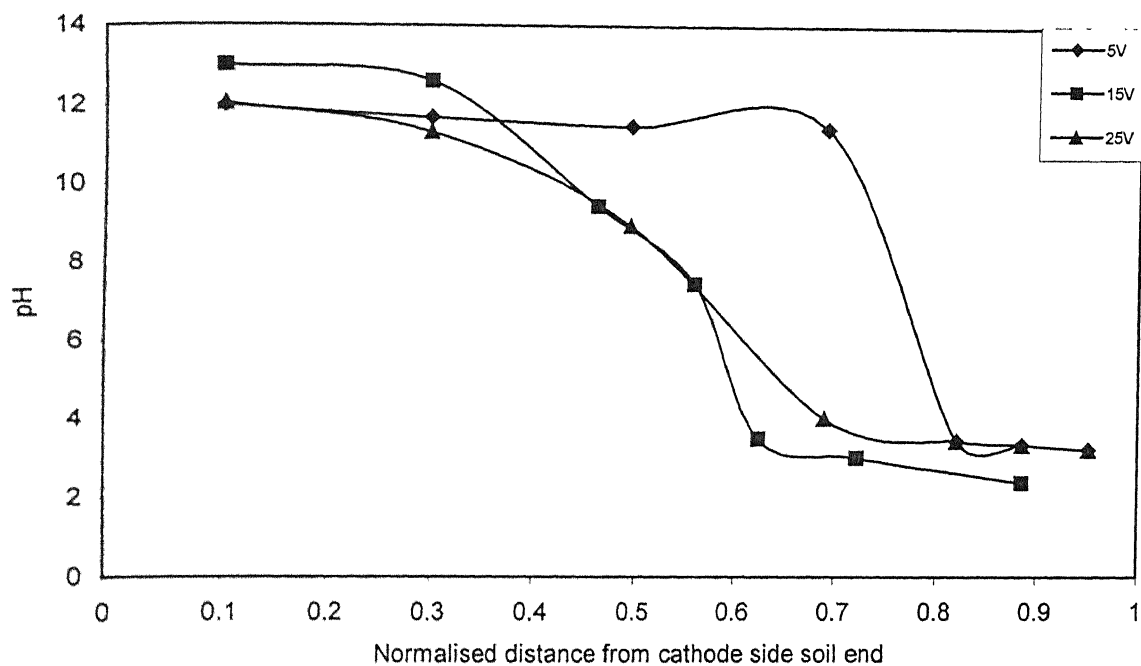


Fig. 4.26. pH distribution profile in Kanpur soil after end of experiment.

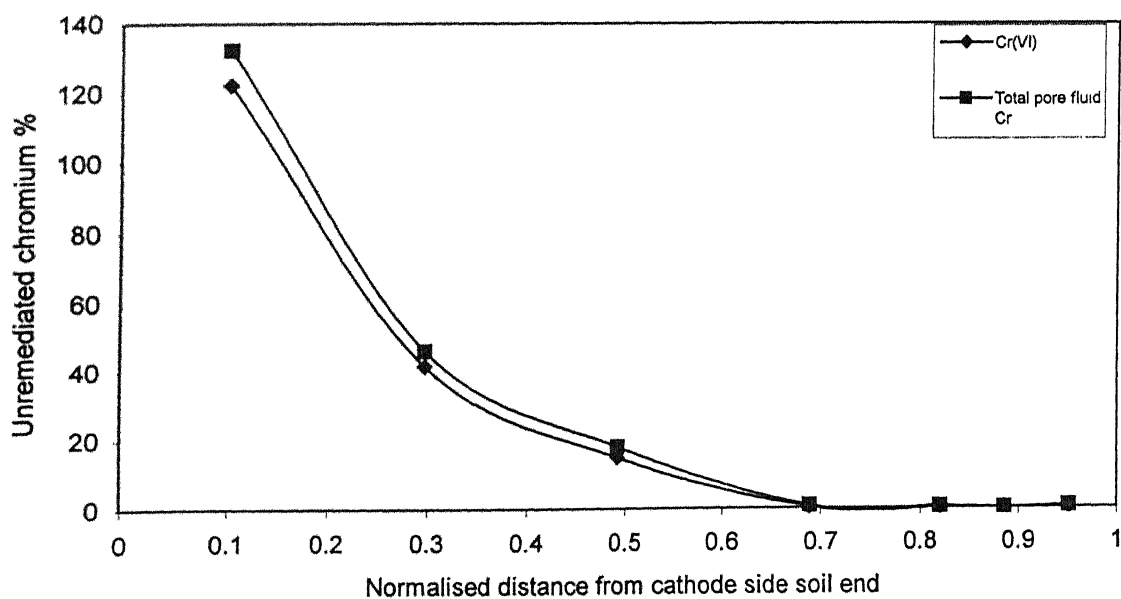


Fig. 4.27. Unremediated chromium distribution in Kanpur soil ( $V = 5$  volts).

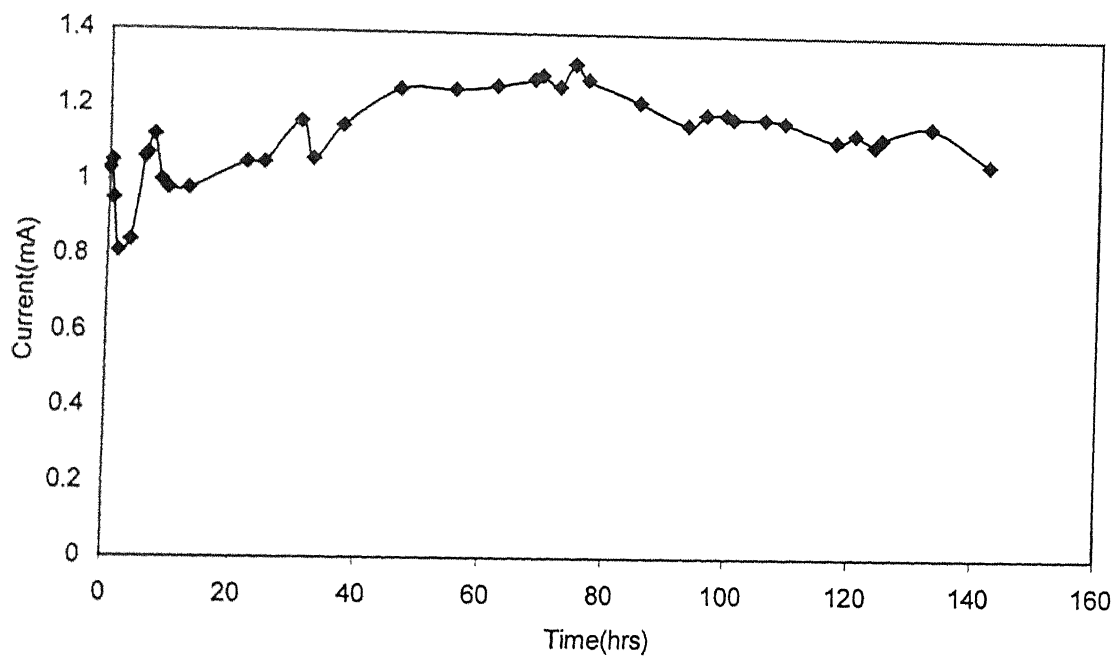


Fig. 4.28. Variation of currents as a function of time of Kanpur soil (V = 5 volts)

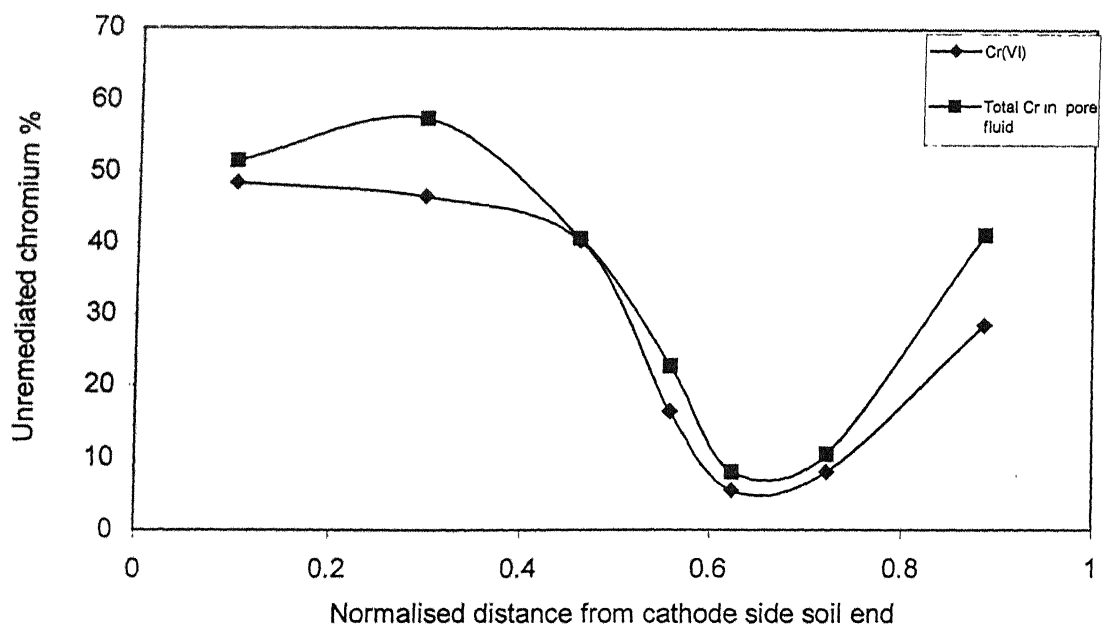


Fig. 4.29. Unremediated chromium distribution in Kanpur soil (V = 15 volts)

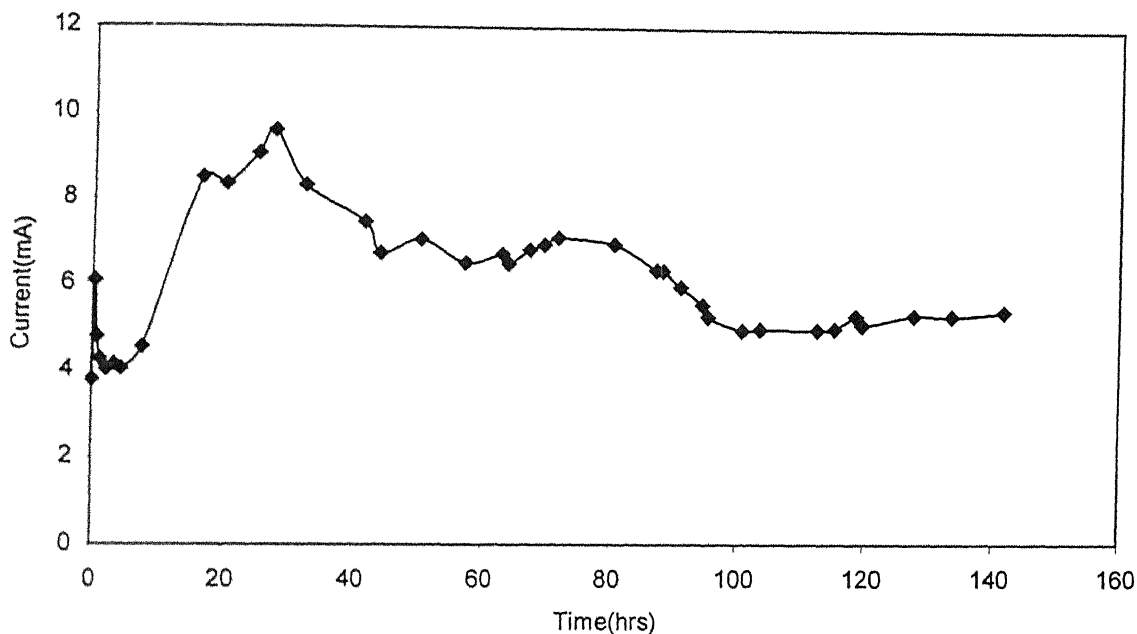


Fig. 4.30. Variation of current as a function of time of Kanpur soil (V = 15 volts).

#### 4.2.4. Effect of Voltage

$$\text{Removal efficiency} = [\text{mg Cr(VI) removal}] / [\text{mg Cr(VI) added in the slurry material}] * 100$$

From Table. 4.2 it is cleared that removal efficiency is high of Kanpur soil at high voltage condition compare to low voltage. At high voltage condition both migrating and electroosmotic flux is high. Adsorption is generally high at high and low voltage condition. These phenomena can be attributed to the fact that the increase in potential enhances the driving force for both electroremediation as well the migration of the acid front.

**Table. 4.2. Mass Balance of Kanpur soil**

Soil	Volts	Days	Wt % removal	Wt % unremediated Cr(VI)	Wt % adsorbed Cr(VI)	Wt % unaccounted Cr(VI)
Kanpur soil	25	6	84.12	0	10	5.88
Kanpur soil	15	6	41.53	50.98	5	2.5
Kanpur soil	5	6	35.57	47.12	12	5.31

Specific power consumption = Total watt-hrs consumed per day/(% chromium removed)

Fig. 4.31 is a plot of power consumption per unit percent chromium removal from Kanpur soil, a measure of energy consumption versus applied voltage. This also shows that increase in applied potential translates into higher power consumption or lower energy efficiency.

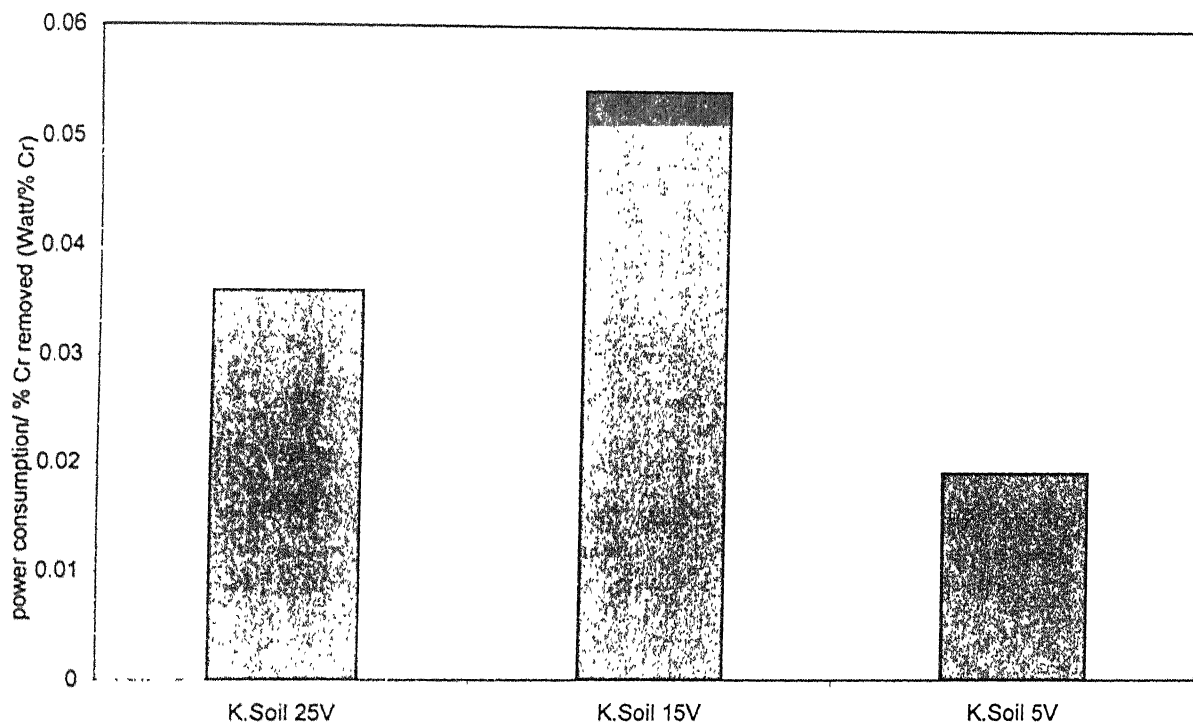


Fig. 4.31. Specific power consumption at different applied voltage of Kanpur soil.

#### 4.2.4.1. Optimum Voltage:

From removal and energy efficiency point of view we are getting two different aspects, application of constant voltage for electroremediation is entirely depends on the two factors. If removal efficiency factor is more important over energy consumption, then higher voltage experiment is better. Reverse will be true, if energy consumption for per mg Cr(VI) removal is the main factor.

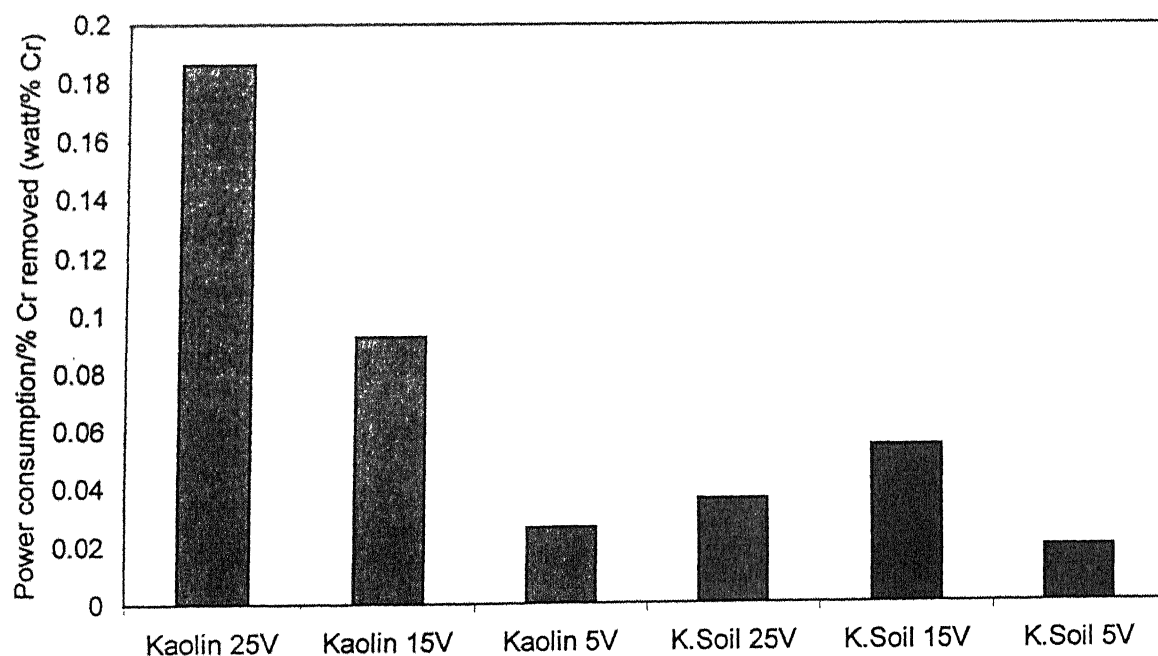
### 4.3. Comparison of Kaolin Vs Kanpur soil

Removal efficiency is high in case Kanpur soil compare to kaolin as shown in Table. 4.3. Adsorption is significant at high voltage condition in case of kaolin but in case of kanpur soil adsorption is high at high and low voltage condition. This phenomenon can be attributed to the fact that the increase in potential enhances the driving force for both electroremediation as well the migration of the acid front.

**Table. 4.3. Mass Balance of Kaolin and Kanpur soil**

Soil	Volts	Days	Removal (Wt %)	Unremediated Chromium (Wt %)	Adsorbed Chromium (Wt %)	Unaccounted Chromium (Wt %)
Kaolin	25	5	36.6	48.92	10.48	4
Kaolin	15	6	31.82	51.85	12.23	4.1
Kaolin	5	6	15.32	74.47	7.006	3.2
Kanpur soil	25	6	84.12	0	10	5.88
Kanpur soil	15	6	41.53	50.98	5	2.5
Kanpur soil	5	6	35.57	47.12	12	5.31

Fig. 4.32 is a plot of specific power consumption per unit percent chromium removal from kaolin and Kanpur soil, a measure of energy efficiency versus applied voltage. From this plot, it is cleared that power consumption for electroremediation from Kanpur soil is less compare to kaolin.



**Fig. 4.32. Specific power consumption at different applied voltage of kaolin and Kanpur soil.**

#### 4.4. Beauty of electroosmotic cleaning process

Results shows that around 85 Wt % Cr(VI) is removed successfully from Kanpur Soil but only 36.6 Wt % Cr(VI) is removed from kaolin as shown in Table. 4.3. This type of results is happened due to the internal different pH of the slurry materials.

In case of kaolin initially electroosmotic flow rate and migrating force is high but 2<sup>nd</sup> one is predominating over first one. After 40 hours both migrating and electroosmotic flux drastically fall down as mentioned earlier. Consequently removal efficiency is very low.

Migrating flux is low in case of Kanpur soil;  $H^+$  ions movement is hindered by the alkaline buffering nature of the Kanpur soil. Consequently high potential drop at the anode side soil end where pH is low compared to other sections, reverse is true for all other sections. Potential drop factor is compensated by the pH factor to maintain uniform electroosmotic flux through out the experiment, except first some hours of the experiment. This is the beauty for electrochemical cleaning of Kanpur soil.

#### 4.5. Fate of Chromium(III)

Figs. 4.1-2, 4.9, 4.17, 4.19 and 4.21 show that some amount of Cr(III) presents in the chamber fluid for both Kanpur soil and kaolin, this is happened due to the rusting of the steel screws, used for tightening the electrodes and rings. Figs. 4.12-14 show that significant amount of Cr(III) presents in the kaolin. Cr(III) presents in anode chamber fluid as cationic and is tried to move to wards slurry materials by migrating force. Cr(III) concentration is nil or very low In case of Kanpur soil slurry materials as shown in Figs. 4.24 and 4.27. This is attributed by Cr(III) presents in cathode chamber. Fig. 4.29 depicts that significant amount of Cr(III) also present in the slurry materials of Kanpur soil. This reverse trend is happened due to Cr(III) also present in anode compartment.

## 4.6. Unaccounted Chromium

Results shows as in Table. 4.3 that 2.5 – 5.88% chromium is unaccounted, this amount of chromium may be adsorbed in porous graphite electrode, filter paper and filter clothes. Unaccounted chromium is different in different experiments that is happened due to different chromium concentration in chamber fluid and experimental error.

## CHAPTER V

### CONCLUDING REMARKS

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1. Kanpur soil and kaolin are cleaned predominately by eletroosmotic flux and electromigrating flux respectively.
2. Initial pH of the slurry material is very important factor for Electroremediation.
3. Removal efficiency is high at high voltage condition.
4. Approximately 85% of Cr(VI), from an industrial dichromate residue, is removed from the local Kanpur soil, but only 36.6% Cr(VI) is removed from kaolin. This is attributed by acid base neutralization.
5. Energy efficiency is low at high voltage condition.
6. Significant amount of chromium is adsorbed in kaolin and Kanpur soil.
7. Adsorption is high in kaolin at acidic pH and insignificant at alkaline pH but in kanpur soil adsorption is high at both acidic pH and basic pH and insignificant at neutral pH.
8. Adsorption is high in kaolin at high voltage condition but reverse is true in kanpur soil.
9. Cr(VI) is transformed to Cr(III) due to presents of reducing element.

## CHAPTER V

### RECOMMENDATION FOR FUTURE WORKS

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The following features can be added in future:

1. Galvanostatic electroremediation of soil contaminated with dichromate lixiviant.
2. Studies of 2 and 3 dimensional experiment in both potentiostatic and galvanostatic ways.
3. Development of mathematical models for optimization of process parameters.

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